

THE EFFECT OF AIR OXIDATION ON SEQUENTIAL SOLVENT EXTRACTION OF THE ARGONNE PREMIUM COAL SAMPLES

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INTRODUCTION

Sequential solvent extraction of coal with a series of increasingly better solvents (Toluene, THF, DMF, Pyridine) has been used to examine the effect of artificial weathering on several Illinois coals. (1) A similar method with a different set of solvents was recently employed by Kister, et al. on a low-rank French coal. (2) In both cases, each extract is soluble in all later solvents and analysis of the entire set of extracts produces more information than extraction with a single solvent. Because extracts so isolated have experienced some fractionation and concentration, FT-IR and GPC analyses of the extracts often reveal subtle changes due to chemical treatment, such as weathering, not obvious from analysis of the whole coals.

The availability of premium coals is an opportunity for many laboratories to study the effects of both coal rank and coal weathering on a variety of properties of the same coals. Changes in sequential solvent extraction, FT-IR spectra of extracts and residues, GPC analyses of extracts, and solvent swelling of residues brought about by weathering of five Argonne Premium Coals are the subject of this paper.

EXPERIMENTAL PROCEDURES

Argonne Premium coal samples were dried to constant weight in an Abderhalden apparatus at 100°C and 0.05 Torr (standard conditions) immediately prior to extraction or oxidation. Samples were oxidized as thin layers, in recrystallizing dishes covered to exclude dust, but permit free circulation of air, at ambient temperature and humidity for at least four months. Weathering coals were stirred once a week to promote uniform air exposure and redried to constant weight before extraction. Sequential solvent extraction of coals in the order: toluene, THF, DMF, pyridine followed the method described previously. (1) Samples of coal and oxidized coal (7-10 g) were exhaustively extracted with purified, Argon purged, solvents in a Soxhlet apparatus, under an Argon atmosphere. Extraction with each solvent was continued until no color was visible in the siphoning solvent for at least ten hours. All extracts and washing solvents were filtered through 0.45 μ m Nylon membrane filters before vacuum evaporation and standard drying to constant weight. Residues plus DMF and pyridine extracts were washed several times with 80% methanol/water to remove those solvents.

Gel Permeation Chromatography (GPC) analyses of all extracts were determined on pyridine solutions (6mg/mL) using a train of three Ultragel columns with pyridine mobile phase. (1) KBr pellets (3.0 mg sample/300 mg KBr) were prepared in an nitrogen flushed glove bag and dried under standard conditions to reduce surface moisture. FT-IR spectra were collected at 2 cm^{-1} resolution on a Nicolet 20-DXB spectrometer. Phenol contents were determined by the Blom acetylation procedure (3) with N,N-dimethylaminopyridine (DMAP) as a catalyst. Volumetric solvent swelling of residues with dry, distilled solvents followed standard methods. (4)

RESULTS AND DISCUSSION

Analytical data for coals, oxidized coals, and two residues are presented in Table 1. Preliminary elemental analyses of the coals are based on many analyses by

several labs, the values for the oxidized coals are from single samples. The well-known problems of comparing such data sets are illustrated by the %C values for fresh and oxidized samples of coals 1, 3, and 4. The expected decrease in carbon content with oxidation is not shown. Additional analyses of both sample sets are needed. Volumetric solvent swelling ratios of extraction residues are listed with the coals they were derived from in Table 1. The effect of oxidation on solvent swelling is both rank and solvent dependent. A decrease in swelling correlates with an increase in cross-linking, either from covalent or hydrogen bonds. Swelling of fresh coals increases and then decreases with rank, as does the extractability reported in Table 2. Total extract yield does not correlate directly with swelling in any single solvent, but swelling ability of the solvent is clearly important in determining extract yield. Differences in swelling between toluene and anhydrous ethanol correlate with oxygen contents of the original coals, showing that ethanol is an hydrogen bond donor in swelling experiments. Except for coal #1, changes in toluene and ethanol swelling caused by oxidation correlate with the change in total extractability and show that room temperature oxidation can cause either a net increase or decrease in cross-linking depending on the rank of the coal.

Phenol contents of fresh coals generally increased with weathering. Liotta(5), using alkylation with NMR and FT-IR spectroscopy to measure phenols, found the phenol content of a Monterey Illinois 6 coal to be close to our result for Argonne #3, but observed no change upon weathering for several months, in contrast to the increases we measured for the coals in Table 1. This may reflect differences between coals or oxidation procedures or it may indicate that the Blom acetylation procedure is counting as phenol other reactive groups in coals through transesterification or anhydride formation. This would cause oxidized coals, which contain esters or acids, to give high phenol analyses. Residues of our oxidized coals usually have fewer phenols than residues of fresh coals.

Sequential solvent extractions are tabulated in Table 2 and summarized in Figure 1. Variations in total yield with rank are consistent with early work by Dryden.(6) In this and previous studies(1), we have shown that total extract yields are reproducible to within $\pm 0.5\%$; that changing the order of extraction to pyridine, toluene, THF, DMF does not change the total extract yield; and that pyridine removes over 97% of all soluble material when it is the first solvent in the sequence. In single solvent extractions with THF or DMF on several Illinois coals, yields equal the sum of the sequential extraction yields for all solvents up through that solvent in the sequence. We believe that each solvent in the sequence can dissolve everything removed by previous solvents plus additional material made soluble by the increased swelling and solvating power of that solvent.

Extracts and residues which have been in contact with DMF or pyridine were washed with 80% methanol/water to remove these solvents. Only for the sub-bituminous coal did the methanol washes extract highly colored material and leave a significant residue ($> 0.1\%$) after evaporation. Small amounts of colloidal material were isolated from the membrane filtration of extracts from oxidized #2 and #3 coals. For material balance purposes, methanol solubles were counted as part of total (but not individual) extracts and colloids as part of residues.

On Figure 1, total extract yields for oxidized coals have been plotted at the carbon values of the fresh coals for comparison. Individual solvent extract yields for fresh coals have been plotted on the same graph to illustrate the variation with rank for each solvent in the sequence. Studies which use single solvent extractability with 'early' solvents such as THF to measure the extent of some reaction within coal risk missing production or loss of material which may be of a size and polarity to dissolve in that solvent but which remains trapped in the coal pores because of the poor swelling characteristics of the solvent.

Of particular note is the unusual pattern of individual solvent extract yields

of coal #1 in contrast to the 'normal' (6) total extract yield for a coal of this rank. This may be due to the low swelling of this coal in the early solvents. Only with the effective swelling solvents, DMF and pyridine, can the potentially soluble material diffuse out of the coal network. FT-IR spectra of extracts (below) support this view. DMF extraction of coal #1 took nearly a month to reach completion because of slow diffusion of extracts from the coal. In general, extraction time correlated with extract yield and solvent viscosity. DMF extractions were always the slowest.

Only the two lowest rank coals showed significant changes in total extract yield after artificial weathering. Previous results with a variety of Illinois coals (1,5) and Bruceton (hVAb) coal (7) led us to expect reduction in extract yield to be more general than observed. Larsen (7) found a significant decrease in pyridine extractability when Bruceton coal was heated at 80°C, in contrast to our results for coal #4. If the different results are due to oxidation temperature, the reactions leading to a decrease in extractability apparently have large free energies of activation. Larsen's values for pyridine solvent swelling of the Bruceton coal showed little change upon oxidation and fall between our values for fresh and oxidized coal #4 (Table 1).

Changes in FT-IR spectra of sequential extracts upon oxidation were much more striking than changes in the spectra of whole coals or insoluble residues, consistent with the idea that sequential solvent extraction fractionates and concentrates mobile material from coal. Smaller, mobile molecules are more reactive and change more upon weathering than the insoluble network. Figures 2 and 3 present FT-IR spectra of the toluene and pyridine sequential extracts from coal #1 (B), oxidized coal #1 (A), and the difference (A-B). The new carbonyl peak at 1722 cm^{-1} is barely visible in the difference spectrum of #1-OX - #1 coal. This new band has been observed previously in oxidized coals and is suggested to be due esters. (8) It is observed in several sequential extracts of coals 1-OX, 2-OX, 3-OX, 4-OX, and 5-OX in this study and is always accompanied by bands near 1260 and 1102 cm^{-1} , consistent with ester formation. The 1722, 1260, and 1102 cm^{-1} bands are more prominent in extracts of higher rank coals. They are small, but visible, in the THF and pyridine extracts of coals 2-OX and 3-OX. That they occur at all in pyridine extracts, produced from coal exhaustively extracted by toluene, THF, and DMF, is consistent with the idea that the superior swelling ability of pyridine is allowing material similar to the toluene extracts to escape.

The difference spectrum of 3-OX (Figure 4) is dominated by a band at 1666 cm^{-1} , which is also present at low intensity in polar extracts of 1-OX, 2-OX, and 5-OX, and possibly as a shoulder in 1-OX, Figure 3. This band was ascribed by previous workers to quinone or related aryl carbonyl functional groups. (8a,9) Many spectra of oxidized coals and their extracts show a single, sharp band at 750 - 725 cm^{-1} . Aromatic C-H bending and mineral matter both produce sharp bands in this region, however these extracts contain less than 2% ash. The source of this band is currently under investigation and, if not an artifact, could serve as a simple marker for weathering.

GPC analyses of the extracts are consistent with Dryden's early observation that molecular size generally correlates with extract yield. (6) Figures 5 - 7 present Molecular Size Profiles of coals #1, #1-OX, and #2. In each profile, GPC traces of all sequential extracts from a coal are plotted together. Profiles for several Illinois coals similar to #3 and #3-OX have been published previously. (1) Comparison of Figure 5 with 6 shows that even though total extract yield was little changed by weathering, a larger fraction is being removed by DMF and this material came from the pyridine extract. Changes in the shapes of the GPC curves indicate that toluene is extracting a broader range of molecular sizes after weathering and that the THF extract of #1-OX contains more oxygenated molecules than the other fractions. GPC curve height is very sensitive to the presence of hydroxyl and carbonyl functional groups. (10) Comparison of Figure 5 with 7 illustrates changes due to rank in both average molecular size and distribution of extracts.

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Table 1 Analyses of Samples (DAF)

Argonne Sample	%C	%H	%N	%S	%O	% Ash	Solvent Swelling in		
							Toluene	Ethanol	Pyridine
#2 ^a	74	5.1	-	0.5	19	8	1.31	1.43	1.68
2-OX ^b	70.68	5.77	0.75	0.28	22.60	10.16	1.61	1.52	1.82
#3	77	5.7	-	5.4	10	16	1.64	1.82	2.31
3-OX	78.09	5.99	1.39	5.52	9.01	16.90	1.51	1.53	2.51
3-Res ^c	76.71	5.84	1.68	6.85	8.92	19.91			
3-OX-Res ^c	76.89	5.55	2.32	6.24	9.00	18.85			
#4	83	5.8	-	1.6	8	9	1.54	1.74	2.76
4-OX	83.31	5.91	1.39	2.26	7.13	10.06	1.56	1.63	2.23
#1	87	5.5	-	2.8	4	13	1.17	1.05	1.31
1-OX	87.29	5.37	1.53	3.00	2.81	11.23	1.59	1.37	1.75
#5	91	4.7	-	0.9	3	5	1.06	1.11	1.10
5-OX	89.72	4.95	1.17	0.21	3.95	4.22	1.02	1.05	1.06

a Preliminary elemental analyses, Dr. Karl Vorres, A N L.

b Air oxidation, ambient temperature and humidity, four months. Elemental analyses for oxidized coals and residues by Galbraith Laboratories, Knoxville, TN. Ash determined by L.C. Warfel, ASTM D 3174.

c Insoluble residue from sequential extraction (Table 2).

Table 2

Sequential Solvent Extraction Yields
Weight %

Argonne Sample	Toluene Extract	THF Extract	DMF Extract	Py Extract	Total Extract	Insoluble Residue	Material Balance
#2	2.16	1.38	1.76	0.34	6.1 ^a	91.8	97.9
2-OX	2.35	0.97	3.52 ^b	0.54	9.0 ^c	86.9	95.9
#3 ^d	7.08	7.76	11.40	0.86	27.1	75.5	102.6
3-OX	5.18	5.08	7.38	0.54	18.2	84.8	103.0
#4	5.80	8.18	10.35	0.64	25.0	76.0	101.0
4-OX	5.72	7.78	10.97	1.18	25.6	73.7	99.3
#1 ^d	0.58	0.16	12.63	7.56	20.9	77.9	98.8
1-OX	1.12	0.19	17.37	1.45	20.1	76.3	96.4
#5	0.40	0.24	0.25	0.30	1.2	100.2	101.4
5-OX	0.37	0.37	0.48	0.28	1.5	96.3	97.8

a Includes 0.44% material recovered from the MeOH/H₂O wash of the residue.

b An additional 1.20% was recovered from the MeOH/H₂O wash of the extract.

c Includes 0.37% material recovered from the MeOH/H₂O wash of the residue.

d Average of duplicate extractions.

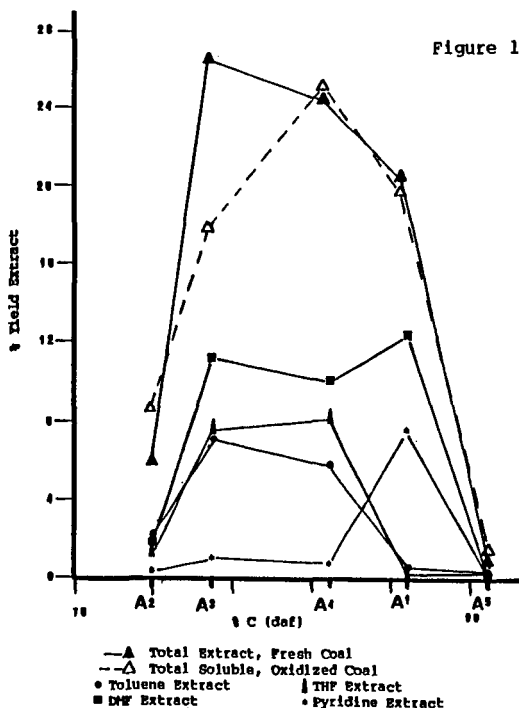


Figure 1 Extraction yield as a function of rank (% C) for Argonne Premium Coals A₁-A₅.

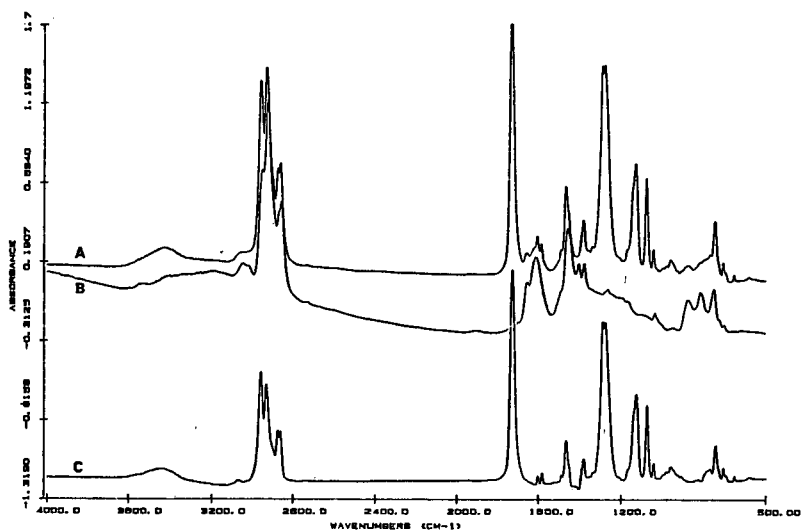


Figure 2 FT-IR spectra of toluene extracts from Argonne #1.
A) Oxidized coal, B) Fresh coal, C) Difference A-B.

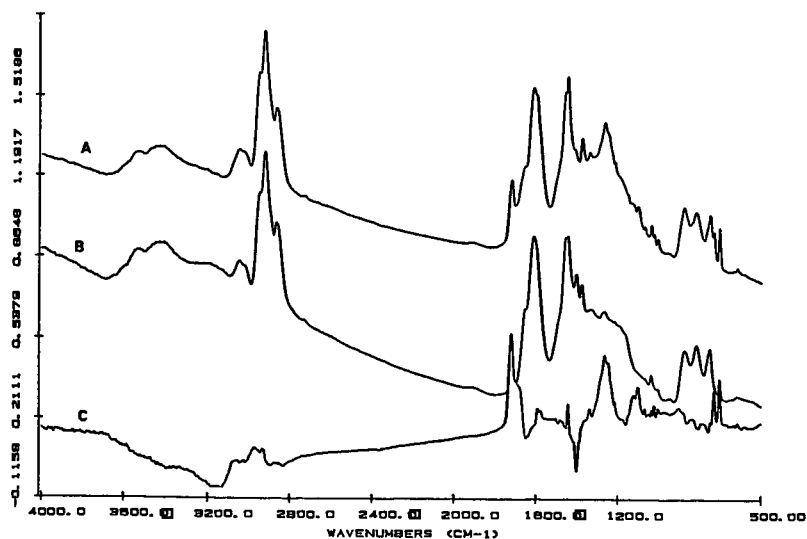


Figure 3 FT-IR spectra of pyridine extracts from Argonne #1.
A) Oxidized coal, B) Fresh coal, C) Difference A-B.

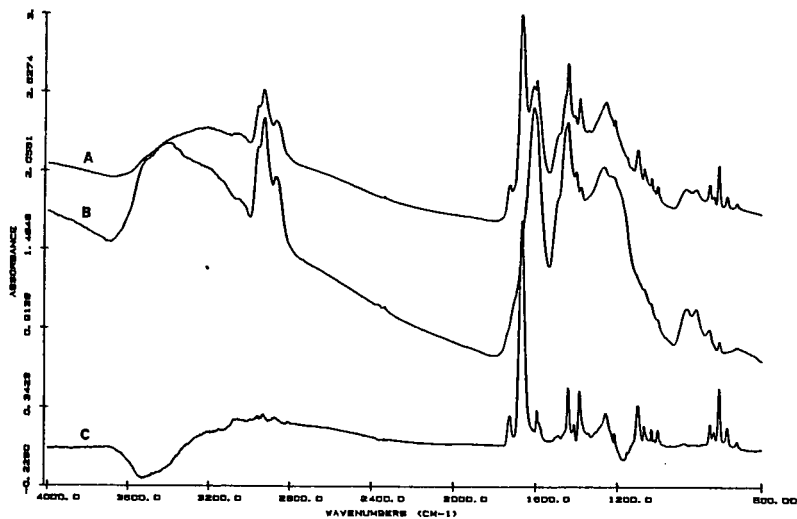


Figure 4 FT-IR spectra of pyridine extracts from Argonne #3.
A) Oxidized coal, B) Fresh coal, C) Difference A-B.

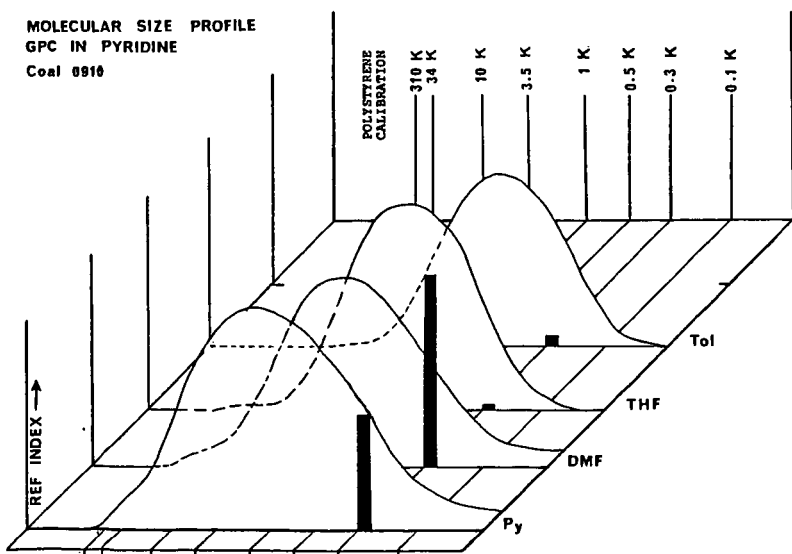


Figure 5 GPC traces from Argonne #1. Vertical bars indicate fraction of total extract removed by indicated solvent.

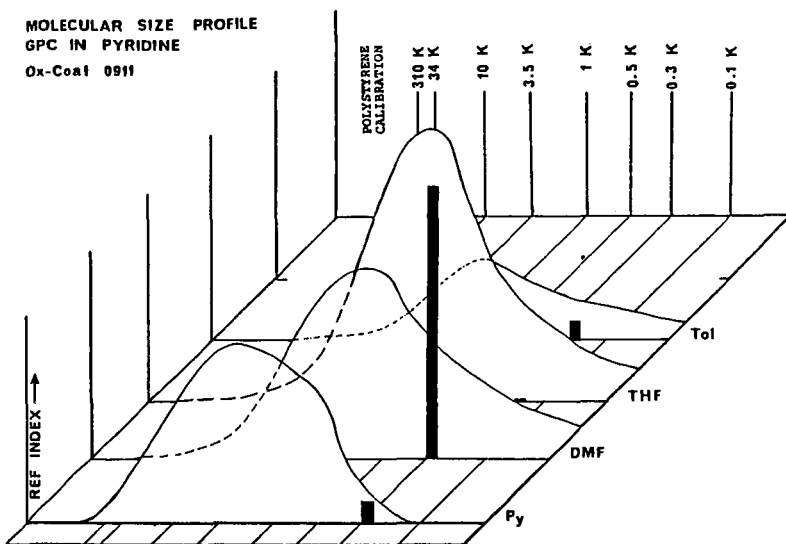


Figure 6 GPC traces from Argonne #1-OX. Vertical bars indicate fraction of total extract removed by indicated solvent.

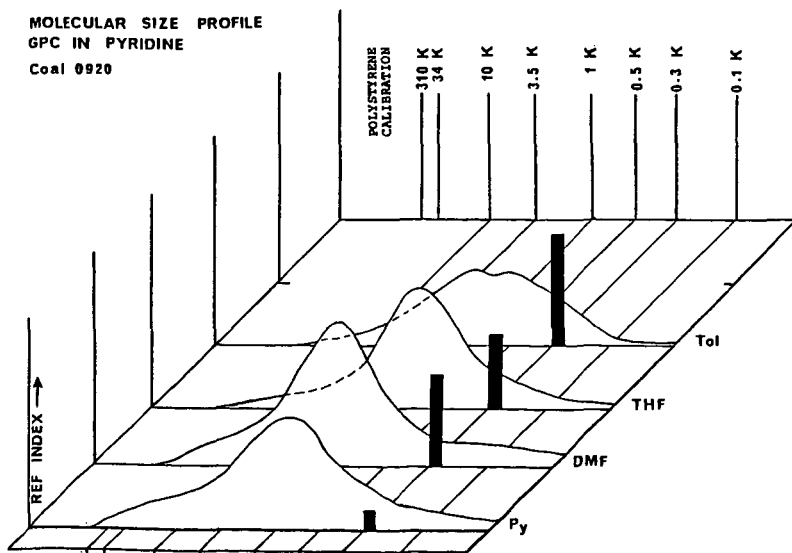


Figure 7 GPC traces from Argonne #2. Vertical bars indicate fraction of total extract removed by indicated solvent.

ATTEMPTED DEVELOPMENT OF A "WEATHERING INDEX" FOR ARGONNE PCSP COALS

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INTRODUCTION

It is well known that weathering has a profound effect on many important coal properties such as coking characteristics, slurry pH, flotability, tar yield, extractability, etc., as well as on coal utilization processes such as combustion, pyrolysis, gasification and liquefaction. However, since coal is a very heterogeneous material and its properties differ according to rank and seam, it is very difficult to define reliable standard values for the degree of weathering. Therefore, most methods for determining the degree of weathering provide relative values and have practical usefulness only if measured values can be calibrated against coal samples weathered under carefully standardized conditions. Since fresh samples from several standard coals are now available from the Argonne Premium Coal Sample Program (PCSP) systematic studies of the weathering behavior of these coals have become practical as well as timely.

In the past, many different attempts have been made to measure the degree of weathering of a given coal sample. One of the more obvious approaches is perhaps to determine the oxygen content by oxidative (1,2), reductive (3,4), or pyrolytic methods (5). Alternatively, oxygen content can be measured directly by neutron activation analysis (6). However, the uptake of oxygen by a given coal can be offset to a significant degree by the concomittant loss of CO₂, CO and H₂O (7), thus making the net increase in oxygen content far from easily predictable. Moreover, most oxygen measurement techniques are notoriously time-consuming and unreliable.

Workers in the coke producing industry have known for a long time that caking properties of coal change dramatically upon weathering. Consequently, they have tried to develop simple and practical methods for determining the degree of weathering. Gray *et al.* (8) suggested an alkali-extraction method as one of several candidates. Lowenhaupt and Gray (9) applied this alkali-extraction method using light transmittance as an index of weathering for high to low volatile bituminous coals. The fact that coal swelling properties change dramatically when a caking coal is weathered presents many potential opportunities for determining the weathering status. Swelling properties of coal can be measured by means of Free Swelling Index (FSI), dilatation, Gieseler fluidity or gas flow resistance tests (10,11). For strongly caking coals FSI is not as sensitive as dilatation or Gieseler fluidity (12,13). In the early stage of weathering, Gieseler fluidity appears to be the most sensitive of the three methods. However, Gieseler values tend to drop to zero after some oxidation time. Under moderate and severe weathering conditions, however, FSI is a good index of weathering, especially in the FSI range between 1 and 4 (14).

Fourier Transform Infrared Spectroscopy is known to show an increase in carbonylic, carboxylic and phenolic groups as well as a decrease of aromatic and aliphatic moieties. Huggins *et al.* (15) proposed the ratio of reflectance in the carbonyl band region to that in the region of the aromatic and aliphatic C-H stretch bands as a possible weathering index.

Thermal analysis methods, e.g., thermogravimetry (TG), as well as analytical pyrolysis techniques (e.g., pyrolysis MS (Py-MS)) also show a strong response to weathering. Izuwara *et al.* (16) used the change of maximum weight loss rate in TG

as a weathering parameter, whereas Jakab *et al.* (17) used time-resolved Py-MS to show that the evolution profiles of several components (carboxylic acids, naphthalenes, methanol, water, etc.) were quite different when coal was weathered.

The Zeta potential of coal particle suspensions in H₂O can also be a good indicator of weathering. Since weathered coal shows poor flotation characteristics, several studies were undertaken to understand this phenomenon in more detail (18-20). In general, weathered coal shows lower Zeta potential values than fresh coal.

Another important feature of weathered coal is its acidic character. Thus, Gray *et al.* (8) suggested coal slurry pH measurement method as one of several candidate techniques for determining weathering status. They reported slurry pH changes from 7.1 to 5.5 for fresh and severely weathered Pocahontas #3 coal, respectively. Hill *et al.* (21) applied this idea to subbituminous (Adaville #6) coal, but added 0.01 wt% surfactant to the slurry in order to enhance the wetting of coal with water. For fresh and moderately weathered (1 to 6 days at 100°C) coals, they reported pH changes from 7.2 to 5.0 and applied this result to coal samples obtained from coal storage piles in order to estimate concomitant btu losses. When coal is exposed to air, oxygen, hydrogen peroxide, nitric acid, potassium permanganate, and other oxidizing agents, mixtures of water soluble acids are formed. For bituminous coal, chromatographic and mass spectrometric studies show that these acids consist mainly of benzoic, phthalic, mellitic and trimellitic acids and their isomers (22). Py-MS results also show an increase of short chain carboxylic acids, e.g., acetic acid, during weathering (23). Moreover, in some cases phthalic anhydrides can be detected by FTIR (24,25) as well as by time-resolved Py-MS (26). If these phthalic anhydrides formed due to weathering can be hydrated to the free acid form, then simple slurry pH measurements can be used as a method of detecting the degree of weathering, as will be shown in this presentation.

Even though some success was reported with the use of slurry pH as an index of weathering, its practical use appeared to be limited to severely weathered coals and some low rank coals. Here we report a modified and improved sample preparation titration method which overcomes these limitations.

EXPERIMENTAL

One to two pound aliquots of 2-4" sized PCSP coals were obtained submersed under water in sealed metal cans. Coals were dried with Drierite in a nitrogen atmosphere overnight and then ground to -60 mesh in a ball mill under nitrogen. Ground coals were transferred to 25 ml polyethylene vials in a glove box filled with nitrogen and stored at -90°C.

Twenty gram aliquots (-60 mesh) of all eight PCSP coals were exposed to a dry air flow (10 ml/min) in a 100 ml glass reactor, at 100°C for 8 days. The Blind Canyon seam coal was weathered for 2, 4, 6 and 8 days in separate glass reactors at 100°C and the Pittsburgh #8 seam coal was weathered at 150°C for 1 and 3 days in order to determine the effects of weathering time and temperature, respectively.

Weathered coal samples were then transferred to a Parr 4745 general purpose digestion bomb. 2.0 g of coal were mixed with 20 ml deionized water and was put in a 23 ml Teflon container and heated to 150°C for 2 hours. Subsequently, the bomb was cooled under tap water for 10 minutes. Next the coal slurry was transferred to a polystyrene beaker for pH measurements. 20 ml of deionized water were used to rinse remaining coal from the teflon container. Resistivity of the deionized water used was more than 16 Meg ohms-cm. pH titrations were performed with a Mettler DL40RC titrator using a 20 ml burette with 0.01 ml titrant (0.01N NaOH) increments.

RESULTS AND DISCUSSION

In earlier weathering studies involving a subbituminous Adaville coal (21), direct pH titration at ambient temperature showed a marked increase in acidity by more than 2 pH units after exposure of the coal sample to air at 100°C for 6 days. However, subsequent pH titration experiments with coals of different rank, including Wyodak (subbit/lignite), Hiawatha (hvb) and Freeport (mvb) coals gave negative or ambiguous results under the same weathering conditions. Nevertheless, Py-MS analyses of the same coals showed a distinct increase in carboxylic and carbonylic functional groups (23). In subsequent Py-MS studies of the weathering behavior of individual macerals (26), strong signals were noted which appeared attributable to anhydrides of phthalic acid and/or other aromatic acids. This provided us with a possible clue to the observed lack of strong pH changes since anhydride formation would effectively remove the acidic protons. Therefore, an attempt was made to re-hydrate the weathered coal samples before carrying out pH titrations. As described under Experimental, rehydration was carried out at 150°C in teflon-lined Parr bombs. As shown in Figure 1 and subsequent figures this procedure was found to be very simple as well as effective in "restoring" the acidity of all weathered coals investigated thus far. Py-MS analysis of the solution extracted during the rehydration procedure, however, indicated that CO_2^+ fragment from acids and acetic acid were the main products, not phthalic acid. Thus more detailed studies are needed to clarify the chemistry behind this method. Figure 1 further suggests that the initial pH can also be a good weathering index for Utah Blind Canyon coal.

Figure 2 shows the effect of weathering duration on pH and repeatability of the method. Clearly, as coal is weathered, more acidic products are dissolved out and therefore lower pH values are obtained. The small differences between repeat analyses on the same weathered coal may be due to temperature variations of the solution. More precise standardization of the method is planned to overcome this problem.

Figure 3 shows the effect of different coal rank, viz. low volatile bituminous (lvb) to lignite. As expected, lower rank coals produce more acidic products during weathering. The difference in the amount of titrant needed to reach pH 8 between fresh and weathered coals reveals even more clearly the effect of rank. Difference spectra obtained by Py-MS analysis of coals of different rank confirmed this observation by showing that structural changes in mvb Upper Freeport coal were only about 30% of those observed in subbituminous Wyodak coal when weathered at 100°C (23).

Possible depositional effects for four coals of similar rank (hvb) are shown in Figure 4. Profound differences in terms of the initial pH as well as the slope of the titration curve are found. Lewiston - Stockton coal has the highest initial pH. This is thought to be due to major differences in depositional environments. Although Lewiston-Stockton coal and Pittsburgh #8 coal show very similar titration curves the difference of the initial pH is most noticeable. In contrast to these coals, Illinois #6 coal produces the most acidic solution. This may be due to its higher sulfur content (and/or higher surface area) than other coals.

The effect of weathering temperature is shown in Figure 5. Note the dramatic pH difference after only 1 day at 150°C as contrasted to up to 8 days weathering at 100°C. This suggests that the weathering temperature may be the most important variable in weathering.

In conclusion, a simple pH titration method based on rehydrating coal slurries with water at 150°C was proved to be a successful way of monitoring weathering effects in all 8 ANL-PCSP coals. For LVB and higher rank coals, however, slurry concentrations should perhaps be increased to compensate for the decreased

susceptibility to low temperature weathering. Further work is underway to elucidate the structural moieties responsible for the observed differences in the shape of the titration curves. Moreover, detailed characterization of the low MW components extracted by the rehydration procedure is expected to yield important information on the underlying mechanisms of the weathering process.

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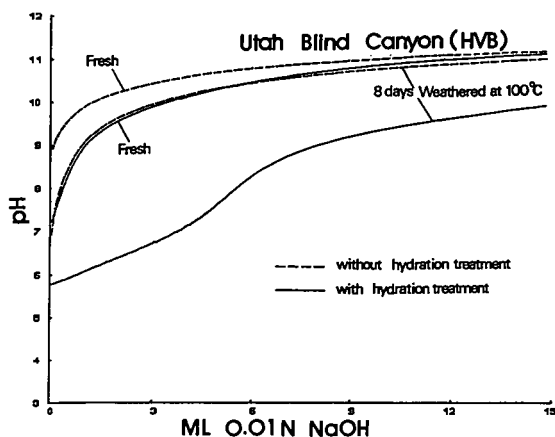


Figure 1. Effect of hydration treatment at 150°C on titration curve.

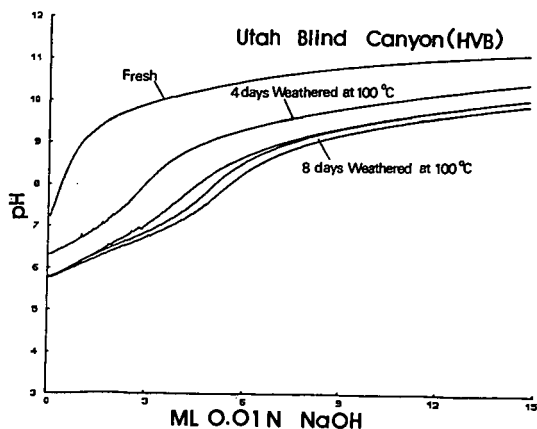


Figure 2. Effect of weathering duration on titration curves. Lower three curves show repeatability for 8 days weathered coal at 100°C.

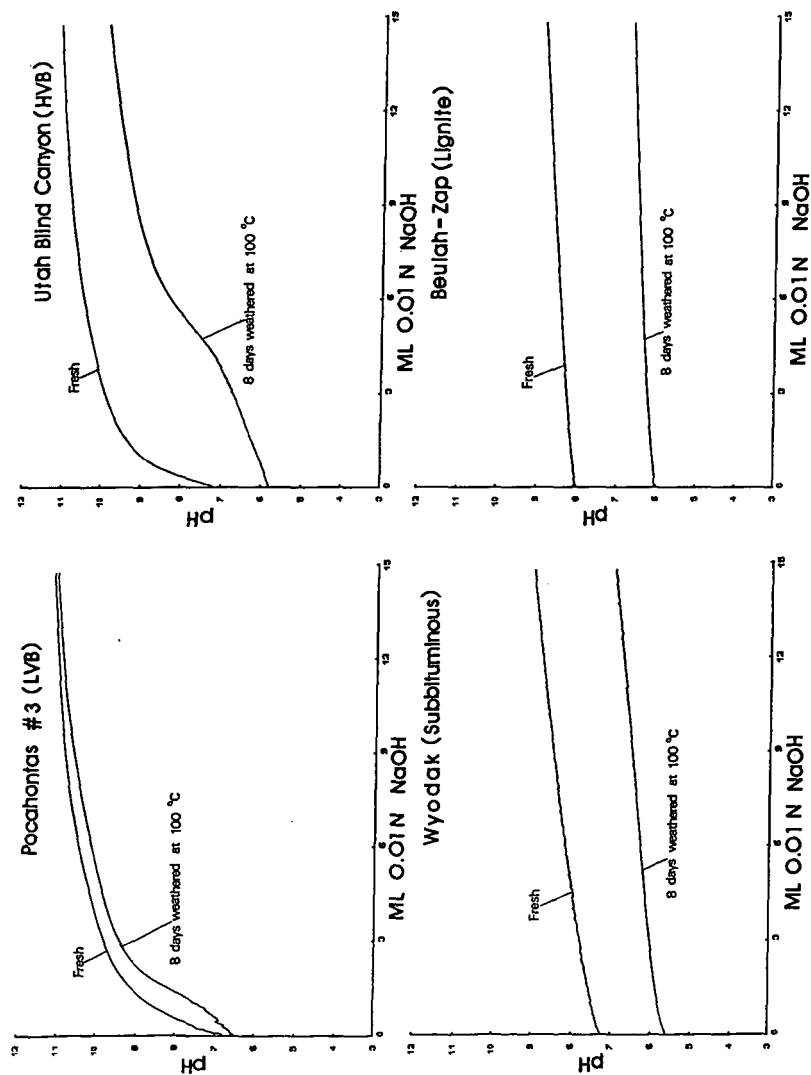


Figure 3. Effect of rank on titration curves.

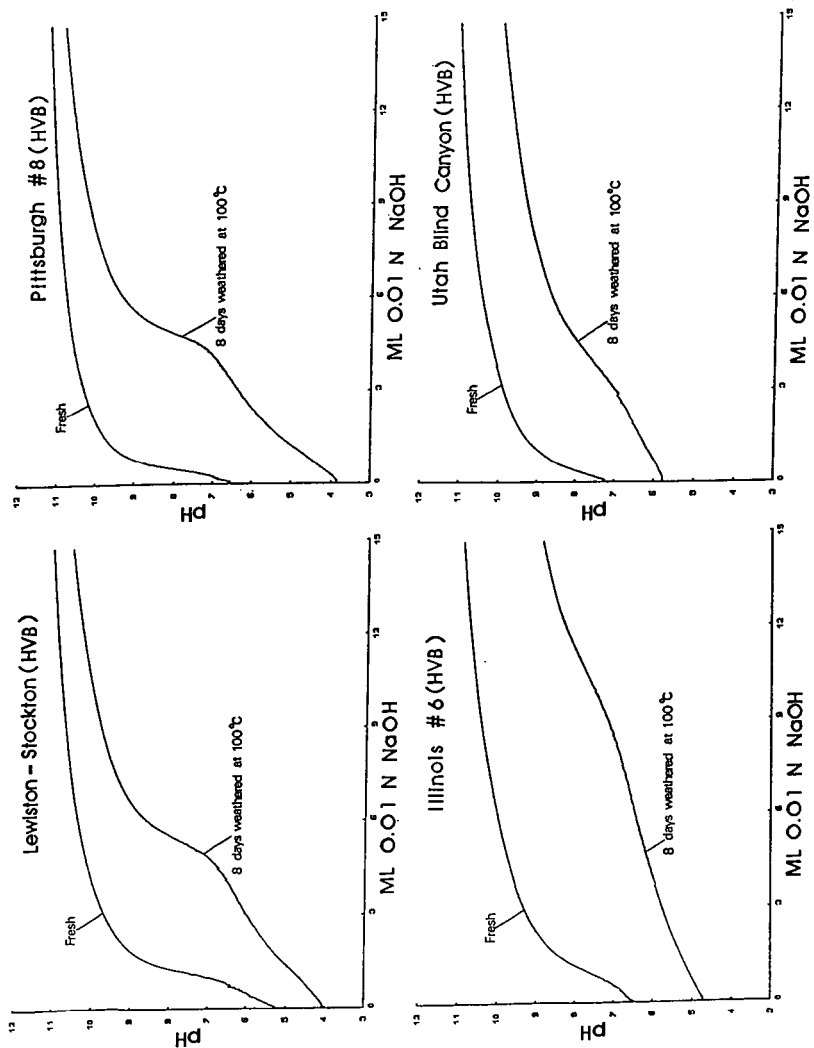


Figure 4. Effect of deposition on titration curves.

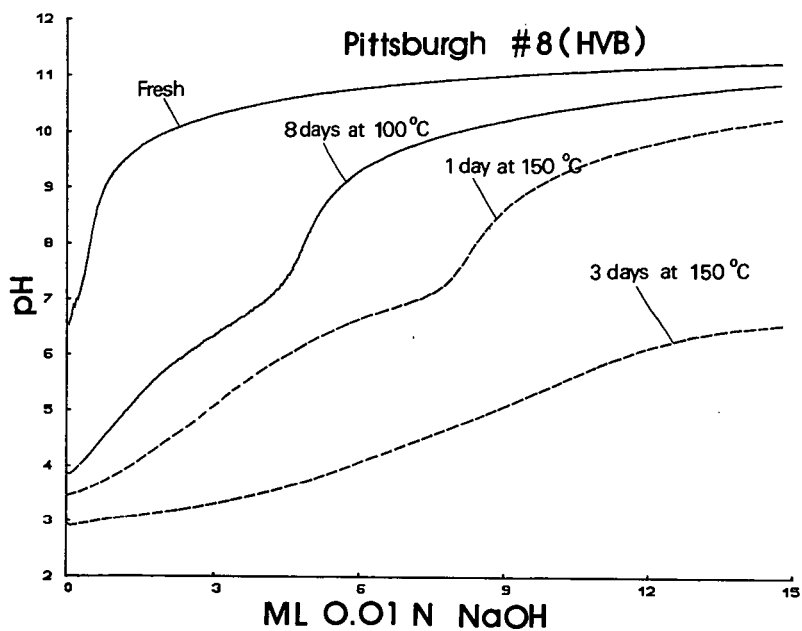


Figure 5. Effect of weathering temperature on titration curves for Pittsburgh #8 coal.

STRUCTURAL INFORMATION FROM THE SELECTIVE METHYLATION OF ACIDIC O-H AND C-H
SITES IN AN ARGONNE PREMIUM COAL SAMPLE*

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INTRODUCTION

With the establishment of the Argonne Premium Coal Sample Program (1), a long-term supply of a limited number of coal samples for basic research has become available to the coal research community. These coals offer the advantage of having been processed and stored under the controlled conditions of relative humidity, temperature, minimum oxygen exposure, etc. Since special care has been taken to insure sample homogeneity, direct inter-laboratory comparisons of experimental results will now be possible. Furthermore, it will now be possible to evaluate the chemical and physical changes which accompany the long-term storage of coal.

RESULTS AND DISCUSSION

Initially, it will be necessary to fully characterize the physical and chemical properties of these samples by a variety of chemical and spectroscopic means. It has been demonstrated that important coal structural information can be established by the application of selective chemical modification reactions to derivatize independently the acidic O-H and C-H sites in coal. For example, it is possible to O-alkylate the phenols and carboxylic acids in bituminous and sub-bituminous coals by reaction with hydroxide and methyl iodide (2) or methyl tosylate (3). Solid (2c,4) and solution (2b) ^{13}C NMR of coal derivatives prepared with C-13 enriched methylating agents have established that indeed O-methylation of phenols and carboxylic acids does occur. On the other hand, it is apparent that significant C-alkylation also occurs under the phase-transfer O-alkylation procedure developed by Liotta (2). For example, as much as 30% of the chemistry is C-alkylation when Illinois No. 6 hvCb is the coal and the alkylation conditions are tetrabutylammonium hydroxide (TBAH) and methyl iodide in aqueous THF (4). The reasons for this phenomenon have never been established. It could derive from ionization and methylation of highly acidic C-H sites or it may indicate competitive O- and C-methylation of phenoxide salts (5). Whatever the reason(s), the results clearly demonstrate that a 'fine tuning' of the reaction conditions towards exclusive O-alkylation is desirable.

We have found that it is possible to 'fine tune' this O-methylation reaction in favor of carboxyl vs phenolic O-methylation by limiting the amount of hydroxide base and replacing the methyl iodide or methyl tosylate with dimethyl sulfate (6). Specifically, the coal is treated with an excess of TBAH. After a specified time

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period (16 h), the excess base is neutralized with HCl. This 'back titration' with acid is monitored, a glass electrode being used to evaluate the pH of the solution. After equilibration, the resulting coal anions are quenched with C-13, C-14 double labelled dimethyl sulfate. The pH dependency of the reaction is evaluated by measuring the total number of introduced methyl groups using C-14 combustion analysis (7). The number of methyl esters in the alkylated coals is defined as the number of hydroxide labile methyl groups measured by hydrolysis (8). Typical results are shown in Table 1 for a nonpremium sample of Illinois No. 6 hvCb. As expected, the degree of methylation is a sensitive function of the solution pH. Over the pH region 2-12, the total number of added methyls increases with an increase in solution pH. More importantly, however, is the observation that the formation of methyl esters is preferred at the lower pH values ($\text{pH} < 7$). This useful property of coal means that the reaction selectivity can be optimized by careful control of the reaction pH. The 'site specificity' of the reaction can be evaluated quantitatively by measuring the ratio, base labile methyls to total methyls. For this particular coal sample, site specificities approaching 70% can be realized when the methylation is carried out at pH 2-7.

An important step in the selective methylation of the acidic C-H sites in coal is the conversion of the phenols and carboxylic acids to their methyl ether and methyl ester derivatives (6,8,9). This is accomplished by the preparation of a pH 12 O-methyl coal using natural abundance dimethyl sulfate as the methylating agent.

To examine the distribution of acidic C-H sites in coal by selective C-methylation chemistry, the pH 12 O-methyl coal is treated in separate experiments with an excess of the conjugate bases of 9-phenylfluorene ($\text{pK}_a = 19$ in THF (10)), fluorene ($\text{pK}_a = 22$ in THF (10)) and triphenylmethane ($\text{pK}_a = 31$ in THF (10)) as their lithium salts (solvent:THF, T:0°C). After a predetermined neutralization time (68 h, typically), the reaction mixtures are quenched with C-13, C-14 double labelled methyl iodide and the products isolated by a series of organic and aqueous extractions. ^{14}C combustion analysis is used to establish the number of $^{14}\text{CH}_3$ groups introduced under each set of reaction conditions. The isolated derivatives are treated sequentially with base and $^{13,14}\text{CH}_3\text{I}$ a total of three times. Previous work (6,9) has established that repetitive treatments are necessary to achieve exhaustive C-methylation. This observation along with the CP/MAS ^{13}C NMR of serially alkylated coal derivatives suggest the chemistry includes the reaction of structural units containing the $-\text{CH}_2-$ group (11).

To facilitate the discussion of the results, we define the number of acidic C-H sites with $\text{pK}_a < 19$ as equal to the number of $^{14}\text{CH}_3$ groups introduced when 9-phenylfluorenyllithium is the base. The number of acidic C-H sites with $19 < \text{pK}_a < 22$ is taken as the difference: number of $^{14}\text{CH}_3$ added with fluorenyllithium minus the number of $^{14}\text{CH}_3$ added with 9-phenylfluorenyllithium. And finally, the number of acidic C-H sites with $22 < \text{pK}_a < 31$ is set equivalent to the difference: number of $^{14}\text{CH}_3$ added with trityllithium minus the number of $^{14}\text{CH}_3$ added with fluorenyllithium.

The structural information available from the application of this chemical approach is illustrated in Table 2 for an O-methyl low volatile bituminous coal, PSOC 1197 (6). Specifically, we can evaluate the distribution of acidic C-H sites in coal as a function of pK_a . In terms of coal structure analysis, this type of information is particularly useful. Since the pK_a values for C-H groups in a variety of organic compounds have been evaluated (10), we can begin to assign a structure to the reactive structural units. For this particular coal, namely

PSOC 1197, we note that the majority of the C-H sites have pK_a values $19 < pK_a < 22$. This observation suggests that structural types such as indenenes and fluorenes as well as those containing C-H bonds adjacent to electron withdrawing substituents (e.g., carbonyl) are important structural features in this bituminous coal, while 9,10-dihydroanthracene structural types are absent. The results from the application of these structural probes to one of the coals from the Argonne Premium Coal Sample Program will be presented during the talk.

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Table 1. Selective O-Methylation of Illinois No. 6 using $n\text{Bu}_4\text{NOH}$
and $^{13,14}(\text{CH}_3)_2\text{SO}_4$

pH	No. $^{14}\text{CH}_3/100$ Coal C		Site Specificity
	Total	Base Labile	
12	4.0 ± 0.4	1.1 ± 0.1	$28 \pm 5\%$
7	1.37 ± 0.01	0.90 ± 0.01	$66 \pm 1\%$
5	0.90 ± 0.08	0.68 ± 0.05	$76 \pm 13\%$
2	0.18 ± 0.02	0.12 ± 0.01	$66 \pm 14\%$

Table 2. Selective C-Methylation of O-Methyl PSOC 1197: The
Distribution of Acidic C-H Sites as a Function of pK_a

pK_a Range	No. C-H Sites/100 Coal C
$\text{pK}_a < 19$	0.06
$19 < \text{pK}_a < 22$	1.8
$22 < \text{pK}_a < 31$	0

COAL DESULFURIZATION BY PHOTOOXIDATION

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ABSTRACT

Oxidative desulfurization of coal has been studied by several workers. These methods primarily involve selective oxidation of organic sulfur to sulfoxide and sulfones, followed by thermal decomposition of the oxidation product.

In this investigation, photooxidation of sulfur functionalities in coal is studied. Finely divided coal, suspended in a solvent, is exposed to radiations of wavelength 300-600 nm using a xenon mercury lamp. The coal sample, is next subjected to hydrolysis to remove the oxidized sulfur from the coal matrix. It is observed that coal desulfurization increased by 7.4%, 3.4%, and 23.7% when coal was photooxidized prior to hydrolysis by water, hydrochloric acid and sodium hydroxide, respectively. Sulfur removed by this technique as sulfonic, sulfurous or sulfuric acid or their salts would be mostly organic in nature.

Introduction

Coal is unquestionably the fuel of the future for the generation of electrical energy but its use gives rise to a number of ecological problems, such as acid mine drainage and air pollution from particulate, sulfur dioxide, and NO_x emissions. Man-made sulfur dioxide and nitrogen oxides emissions in the U.S. are estimated to be over 40 million ton/year. Coal-fired utility power plants account for 55% and 27% of all the man-made sulfur dioxide and nitrogen oxides emissions, respectively in the United States. Sulfur dioxide emissions appear to acidify fresh-water lakes located in acidic soil areas whereas nitrogen oxides emissions appear to kill trees. As U.S. environmental groups become more aware of the tree losses in the Appalachian Mountains, reduction of nitrogen oxides emissions in existing coal-fired utility boilers is expected to be a critical issue.

There are many acid rain control technology options for existing large coal-fired electric utility boilers, namely

- (i) switch to low sulfur coal or natural gas,
- (ii) coal cleaning,
- (iii) flue gas treating,
- (iv) limestone injection multistaged burning,
- (v) fluidized bed combustion, and
- (vi) coal gasification.

The first three options are commercially proven techniques. Coal cleaning reduces only small percent of sulfur as it removes only pyritic sulfur. Sulfur and nitrogen reduction potentials using the flue gas treatment technique are high but the capital and operating retrofit costs are exorbitant. Consequently, there is still a need for an efficient and inexpensive coal desulfurization technique which utility companies could readily use.

In this paper, desulfurization of coal using a photooxidation technique is discussed. Coal samples exposed to radiation of wavelength 300-600 nm using a xenon mercury lamp are subsequently analyzed for sulfur content.

Scientific Rationale for Photo Desulfurization of Coal

Coal is a highly heterogeneous solid originating from plant remains. It contains, in varying amounts, essentially all elements of the periodic table combined into nearly all of the minerals normally present in the earth's crust. In other words, coal is a complex mixture of organic and inorganic compounds in which the organic matrix comprises most of the coal weight. Organic coal matrix can be viewed as a complex macromolecular structure containing the classical organic functional groups such as carbonyl and hydroxyl, aromatic and heterocyclic ring units, and aliphatic bridges.

Coal structure and processing have been the subject of intense research for several years. The exact chemical structure of organic coal matrix varies and is not completely understood. However, enough information is available on the nature of sulfur containing functional groups in organic coal matrix. The organic sulfur in coal can be categorized into one of the functionalities such as thiol, sulfide, disulfide, thiophene, benzothiophene, and dibenzothiophene.

Desulfurization of coal has been investigated by several workers (1,2). They have used techniques such as oxidation (3-6), chlorinolysis (7-8), electrolysis (9), etc. All these methods essentially oxidize sulfur in coal. There are other methods reported in the literature involving hydrogenolysis, hydrolysis, etc. It is observed that among the organic sulfur functionalities, removal becomes increasingly difficult in the order thiolic < sulfide < disulfide < thiophenic < benzothiophenic < dibenzothiophenic. As the complexity of the sulfur containing functionality increases the selectivity of desulfurization, without affecting the rest of the coal matrix, becomes difficult. For example, the selectivity of hydrodesulfurization is reduced whenever the π -electrons of sulfur are in resonance with π -electrons as in the cases of thiophene, benzothiophene, etc. This leads to competing hydrogenolysis of the carbon-carbon bonds since the energies of carbon-sulfur and carbon-carbon bonds become practically identical due to resonance (10). It has been reported that atmospheric weathering leads to desulfurization of coal which can be due to the combined effect of air oxidation and photo-oxidation. However, the authors have not presented any mechanism or photonic role for this process (6).

It has been suggested that accompanying the oxidation of the sulfur to sulfone, the bond energy between the carbon and the sulfur is reduced on the average by 5.2 kcal/mole for aliphatic sulfides and by 11.8 kcal/mole for aromatic sulfides and thiophenes. Thus, the selectivity of decomposition at the sulfur-carbon bond is increased (3).

Oxidative desulfurization of coal has been studied by several workers (1-8). These methods primarily involve two steps: (1) selective oxidation of organic sulfur to sulfoxide and sulfones as shown below and (2) thermal decomposition of the oxidation product expelling sulfur dioxide.

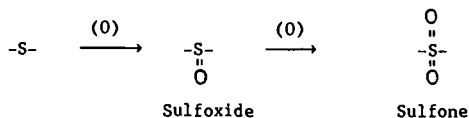


Photo-oxidation of Sulfur in Coal

No work is reported on the photochemical oxidation of coal. It is important to understand how the coal molecule would react in the presence of light and air. Coal due to its strong absorption of the entire visible spectrum has black color. It is also well known that coal has a complex aromatic structure with polyaromatic nuclei capable of absorbing light in the visible region. Attached to these are the sulfur atoms. The n -electrons on sulfur can resonate with the aromatic π -cloud. Hence, in the presence of light the n, π^* transition is also feasible which would affect the bonding properties of sulfur. This might lead to either electron deficient sulfur linkage or formation of diradical or free radicals. Due to the complexity of coal structure it is difficult to theoretically predict the exact course of reaction from the excited state.

There is enough literature evidence that oxygen in air attacks the organic sulfur compounds photochemically (11). Extending the mechanism of photo-oxidation of sulfur compounds to coal, two courses of reaction can be predicted. One of them could be the formation of free radical/diradical center at sulfur from the excited coal molecule and subsequent oxidation and hydrogen abstraction leading to oxidized sulfur functionalities such as sulfonic acid. The second one would be the attack of sulfur center by excited molecular oxygen, namely, singlet oxygen, if the reaction conditions are conducive to the production of singlet oxygen. Either of these mechanisms would cause the formation of sulfoxides, sulfones or sulfonic acids depending upon the reaction conditions. Hence, it is safe to predict that the organic sulfur functionalities in coal could be oxidized in the presence of oxygen and visible light.

By this photo-oxidation treatment the sulfur in coal would remain in an oxidized form. The next step would then be to eliminate the oxidized sulfur from the coal matrix. This can be achieved by subjecting the photo-oxidized coal to hydrolysis. This procedure is reported to be used in other chemical desulfurization techniques also. It is envisaged that most sulfur removed by this technique as sulfonic, sulfurous or sulfuric acid or their derivatives would be organic in nature.

Experimental Set-up and Procedure

Finely crushed coal was suspended in 95% ethanol and kept agitated by bubbling oxygen at such a rate that the coal particles were not allowed to settle down. Also, oxygen bubbling would facilitate the removal of sulfur by oxidation. The coal slurry was subjected to photolysis in an internally lighted reaction vessel. Methylene blue was used as a sensitizer for the production of singlet oxygen. The photo-oxidized coal was washed thoroughly with ethanol to remove the dye and the ethanol was separated by centrifugation. Next, the coal was dried at 110°C for 8 hours. A portion of the photo-oxidized coal was subjected to hydrolysis either in boiling water or by refluxing with solutions of HCl or NaOH. Reference coal was also hydrolyzed with water, acid or base under the same conditions employed for photolysed coal in order to study the effect of photolysis. The samples were analyzed for their sulfur contents. The experimental conditions are summarized in the following Table 1.

Table 1: Experimental Conditions

Coal	Illinois No. 6, Bituminous		
Slurry Concentration	2% in coal and 0.1% in methylene blue		
Hydrolysis Conditions	2% in coal; reflux; 6 h.		
Parameters	Set I	Set II	Set III
Particle Size	74 micron	44 micron	44 micron
Solvent	95% Ethanol	95% Ethanol	95% Ethanol
Reactor	Internal	Internal	Internal
Sensitizer	Methylene Blue	Methylene Blue	Methylene Blue
Radiation	350-550 nm	300-600 nm	300-660 nm
Light Intensity	45 Watts	450 Watts	450 Watts
Reaction Time	10 h.	16 h.	16 h.
Hydrolysis Medium	Water	1 N HCl	1 N NaOH

Results and Discussion

The sulfur contents of the coal samples are presented in Table 2.

Table 2: Sulfur Contents of Coal Samples

Sample	Set I			Set II			Set III		
	Run 1	Run 2	Mean	Run 3	Run 4	Mean	Run 5	Run 6	Mean
Reference	3.92	3.86	3.89	4.56	4.51	4.54	4.56	4.51	4.54
Light Unhydrolysed	3.83	3.80	3.82	4.65	4.45	4.55	4.65	4.45	4.55
Dark Hydrolysed	3.66	3.77	3.72	3.88	3.94	3.91	4.18	4.50	4.34
Light Hydrolysed	3.45	3.42	3.44	3.88	3.60	3.74	3.32	3.22	3.27

Table 3: Percent Sulfur Reduction

Reaction	Set I	Set II	Set III
Dark Hydrolysis	4.5	14.9	4.2
Light Hydrolysis	12.0	17.4	27.8
Photonic Advantage	7.4	3.4	23.7

The desulfurization based on total sulfur is on the average higher by 7.4% (Set I, Table 3) when hydrolysis is conducted by refluxing with water if coal is subjected to photolysis prior to hydrolysis. In other words, the desulfurization increased by about 7.4% as a consequence of photooxidation. It is also seen from Table 3 that photonic advantage increased on the average by 23.7% (Set II) if hydrolysis is conducted in boiling sodium hydroxide solution. However, with acid hydrolysis the photonic advantage is very low (3.4%; Set II, Table 3).

The probable mechanism of desulfurization is the oxidation of some of the organic sulfur functionalities such as sulfide and thiol to sulfoxides, sulfones and sulfonic acids and subsequent hydrolysis of these functional groups. A strong base such as sodium hydroxide would eliminate sulfinic acid from the sulfones and with some difficulty from the sulfoxides while hydrochloric acid would convert the sulfoxide to the original sulfide. It is to be noted that pyritic sulfur would also be affected by hydrolysis though the photolysis might not have significant influence on the removal of pyritic sulfur.

Conclusions

These results show a definite photonic advantage in desulfurization of coal. However, the understanding of the mechanism of desulfurization, nature of functional groups that are affected by photolysis, role of pyrite in modifying the excited state reactivities, influence of reaction medium and optimization of desulfurization conditions need further study.

Acknowledgment

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THE EFFECT OF HEATING RATE AND HOLD TIME ON PRIMARY COAL PYROLYSIS PRODUCT DISTRIBUTION

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Introduction

The study of primary pyrolysis reactions in coals is complicated by the number of secondary effects that must be considered. In particular, secondary volatile-cracking reactions are likely to occur with most pyrolysis techniques for low heating rates (eg. Fischer Assay, Gray-King, thermobalance), which use a relatively large coal sample and allow the volatiles to remain in the heated zone for extended periods. A well-dispersed sample of fine coal must, however, be used to achieve high heating rates (eg. as in a fluidised bed or wire-mesh reactor). This has made it impossible to determine whether the increases in volatile yields noted in many fast heating rate studies (probably the best-known of which is the work by Howard and associates at MIT using a wire-mesh apparatus (1)) were due entirely to a reduction in secondary char-forming reactions, or were at least in part an effect of the heating rate itself. The MIT apparatus used a pulse of direct current to heat the sample holder and the lowest heating rate that could be obtained was about 100 K/s; in any case slow heating experiments might also have been affected by secondary reactions, because volatile products were allowed to circulate freely in the same vessel as the hot wire-mesh. Both of these problems have been addressed, though not always together, in subsequent studies (eg. 2,3,4,5,6), but a systematic examination of the effect of time/temperature history under conditions where secondary reactions would be at a minimum appears to be lacking. It was therefore proposed to construct a wire-mesh apparatus which could cover virtually any time/temperature history and provide for rapid removal of volatile products as part of a study on fundamentals of coal pyrolysis and hydropyrolysis funded by the UK Science and Engineering Research Council (GR/D/06582). Although work has concentrated on British coals, the wealth of published data available for US coals made it essential to test some of these for comparison. These trials, with samples from the Argonne Premium Coal (APC) Sample programme, have shown a general increase in volatile yield with heating rate that does not appear to be due to secondary effects. This suggests that more complex interactions occur in pyrolysis than has sometimes been considered.

Sample preparation

To avoid loss of particles through the wire-mesh sample holder all coals were screened to 100-150 microns. The Pittsburgh#8, Illinois#6 and Pocahontas#3 samples were all obtained as -100 mesh and were screened without further treatment. The Wyoming subbituminous sample was originally -20 mesh and was ground gently by hand in air to all pass through a 150 micron sieve. After screening, coals were dried overnight at 105°C in a nitrogen-purged oven and stored under nitrogen until required. A large amount of fines had to be rejected from all the original samples; this would seem to be a general problem for any experiment requiring sieved coal as it may result in selective enrichment with certain petrographic constituents. An agreement to establish standard sub-fractions of sized coal would be welcome.

Apparatus and experimental procedure

principal features of the apparatus, shown in Fig.1, are a sweep gas flow through the wire-mesh sample holder and a feedback temperature control system using alternating current. The sweep gas, helium flowing at 0.1 m/s, gives a mean volatile residence time within the sample holder of less than 2 ms. Five to ten milligrams of coal are spread in a 12 mm diameter circle at the centre of the sample holder, less than monolayer loading. The sample temperature is defined as the average from two chromel/alumel thermocouples, at the centre and approximately 1mm from the edge of the coal sample, formed from wires inserted through the mesh. Typically, temperatures across the sample are within 20 K of the average and the average is less than 10 K (or 20ms in time at high heating rates) from the target control value. Tar can be caught in a pre-weighed sinter trap cooled with liquid nitrogen which is then heated to 50°C for 30 minutes in air and re-weighed. More details of the apparatus will be available elsewhere (7).

Results and discussion

Fig.2 shows variations with peak temperature in total volatile yields from Pittsburgh#8 coal at 1000 K/s and 1 K/s with zero hold time, and at 1000 K/s with 30 seconds hold time. The reactor geometry, gas flow rate etc. are identical for all runs. With zero hold time, volatile yields for the two heating rates follow different trends, and the higher heating rate yield is below that for slow heating up to about 700°C, after which the 1 K/s yield reaches a plateau at about 42% while the 1000 K/s yield continues to rise to about 48% at 950°C. It could thus be concluded that increasing the heating rate would give either lower or higher yields depending on the peak temperature. At 30 seconds' hold, however, the volatile yields for the two heating rates follow similar trends, and the higher heating rate gives greater weight losses at all temperatures above 400°C. This suggests that provided pyrolysis reactions are allowed to run to completion higher heating rates give higher primary volatile yields.

Runs with Pittsburgh#8 at 1,10,100 and 1000 K/s to 700°C with 30 seconds' hold using tar trapping, plotted in Fig.3, confirm the trend of higher volatile yields with faster heating and indicate that the rise in total volatile yields is due mainly to an increase in tar production. Such differences might be caused by more rapid removal of tar by gas entrainment at the higher heating rates, leaving less time for char-forming reactions. Experiments under vacuum at 1 K/s and 1000 K/s to 700°C were therefore made, with the expectation that if evaporation was a limiting step at low heating rates the 1 K/s yield would increase by more than the 1000 K/s yield. In fact the opposite was observed: the 1 K/s volatile yield increased by about 2% while the 1000 K/s yield went up by about 4%. Under vacuum the 1000 K/s samples swelled much less, suggesting that some plasticising/swelling agent was being removed. The 1 K/s samples never swelled, but were fused. It was also considered that slow heating might be allowing time for slight oxidation of the sample by adsorbed gases, or even the trace of oxygen (less than 2 vpm) in the helium gas supply, and that this enhances subsequent tar-precursor polymerisation reactions. Trials on a UK coal indicate, however, that pyrolysis yields at both high and low heating rates are not sensitive to the level of trace oxygen in the sweep gas.

Comparison with published data for Pittsburgh#8 coal (1,4,8), mostly for 1000 K/s and zero hold, showed that while the maximum volatile yields above 800°C were comparable, reported variations in yield with

temperature fell both above and below the zero hold line in Fig.2. Since the cooling rate in these previous experiments varied from about 10^2 to 10^4 K/s its effect was examined but, as Fig.4 shows, at 600°C yields are not sensitive to cooling rate above 100 K/s. Subsequent experiments demonstrated that the hold time at 600°C is an important factor, however, and the results in Fig.5 show that one second suffices for almost complete devolatilisation. This, together with the steepness of the Fig.2 1000 K/s zero hold curve around 600°C , suggests that experimental variations in the time that the coal is held at 600°C or above are more important than the length of time spent at lower temperatures during cooling. Uncertainties in temperature measurement are possible in cases where, to avoid interference from the heating current, the thermocouple had to be electrically isolated from the sample holder (1) or the junction placed away from the surface (4). The local effect of the thermal inertia of the coal sample itself, reported by Freihaut and Seery (8), could also lead to the temperature being overestimated by perhaps as much as 100°C if the loading near the thermocouple was not representative. As far as possible these errors have been minimised in this apparatus since the sample holder is part of the thermocouple circuits and the coal sample is held around the thermocouples. The temperature of the coal is not, and cannot, be measured directly, however, nor can variations in temperature away from the thermocouples be detected, so experimental scatter can still be significant in regions where yield is a sensitive function of temperature. This is not the case for the conditions used to establish the effect of heating rate as Fig.2 shows, and it is therefore unlikely that errors in temperature measurement could be responsible.

Volatile yields from Illinois#6 and Wyoming subbituminous coals were also found to increase with heating rate, but the yield from the Pocahontas#3 sample showed little or no variation. Results for heating rates between 1 and 1000 K/s are shown in Fig.6.

Conclusions

When secondary effects are minimised, an increase in heating rate from 1 to 10^5 K/s will increase pyrolysis yields from a number of coal types provided that sufficient time is allowed at peak temperatures. The extra volatiles are mainly tars, suggesting either a reduction in polymerisation reactions among tar precursors and/or an increase in tar precursor production due to a greater concentration of reactive species within the coal mass. One coal tested showed little or no effect of heating rate, however, and this, together with the absence of more abrupt variations in volatile yields with heating rate for the other coals, probably means that only a portion of the potential volatile-forming pathways in coals are being affected.

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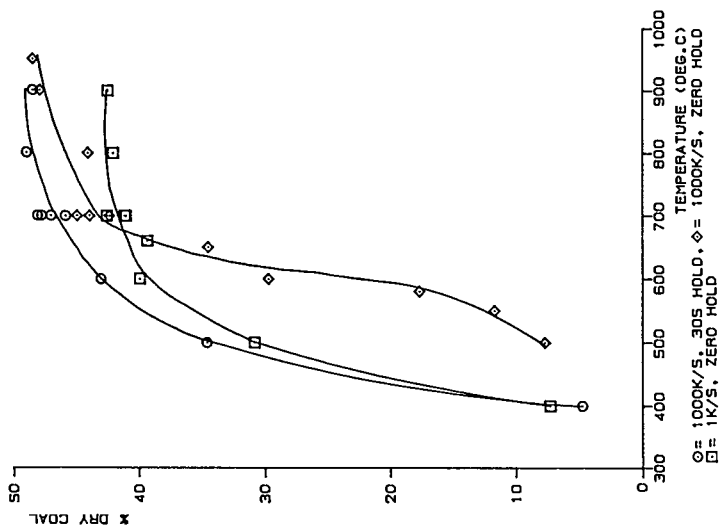


FIG.2 PYROLYSIS YIELDS FROM PITTSBURGH#8
EFFECT OF TIME/TEMPERATURE HISTORY

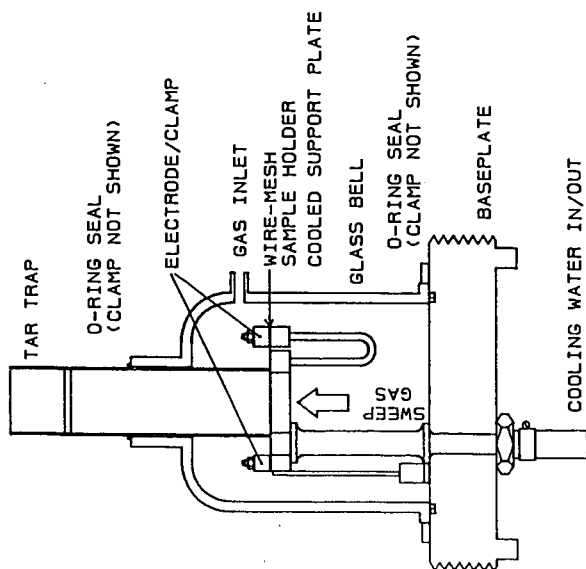


FIG.1 WIRE-MESH APPARATUS

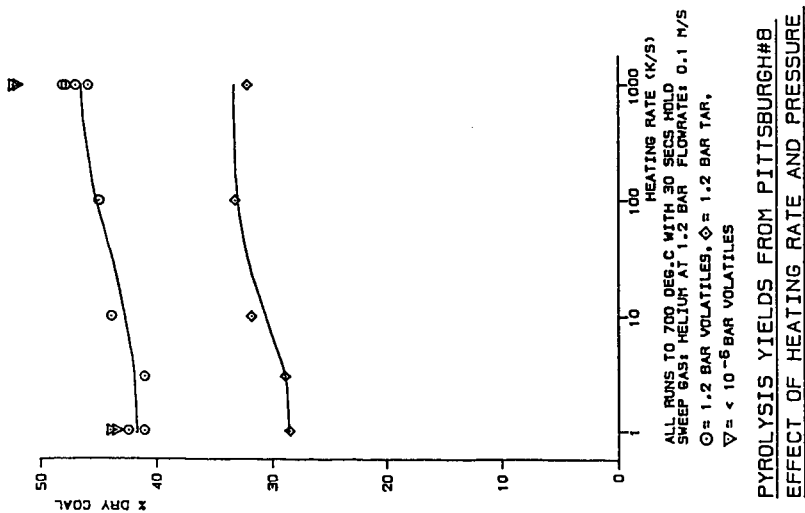


FIG.3 PYROLYSIS YIELDS FROM PITTSBURGH#8
EFFECT OF HEATING RATE AND PRESSURE

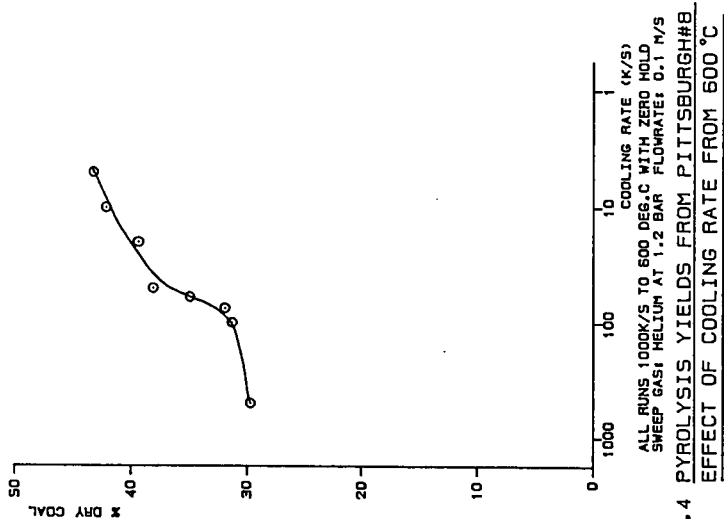
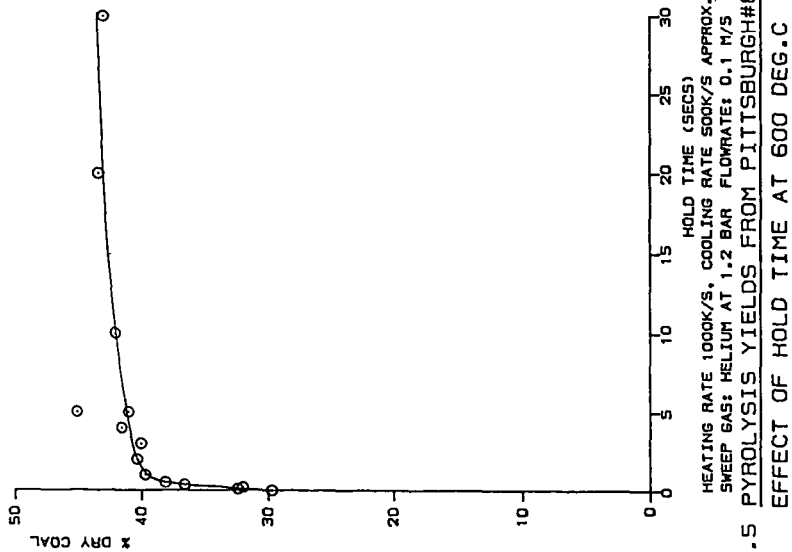
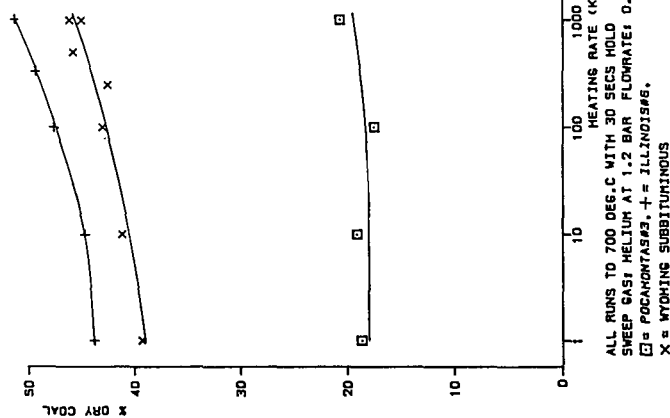


FIG.4 PYROLYSIS YIELDS FROM PITTSBURGH#8
EFFECT OF COOLING RATE FROM 600 °C



HEATING RATE 1000K/S, COOLING RATE 500K/S APPROX.
 SWEEP GAS: HELIUM AT 1.2 BAR FLOWRATE: 0.1 M/S
 FIG.5 PYROLYSIS YIELDS FROM PITTSBURGH#8
 EFFECT OF HOLD TIME AT 600 DEG.C



ALL RUNS TO 700 DEG.C WITH 30 SECS HOLD
 SWEEP GAS: HELIUM AT 1.2 BAR FLOWRATE: 0.1 M/S
 □ = POCAHONTAS#3, + = ILLINOIS#6,
 X = WYOMING SUBBITUMINOUS
 FIG.6 EFFECT OF HEATING RATE ON VOLATILE YIELDS
 FROM ARGONNE PREMIUM COAL SAMPLES

SPECTROSCOPIC CHARACTERIZATION OF ARGONNE PREMIUM COALS AND SHORT RESIDENCE TIME LIQUEFACTION PRODUCTS

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ABSTRACT

Illinois No. 6 (high volatile bituminous), Pittsburgh No. 8 (bituminous), Wyoming Subbituminous, Pennsylvania Upper Freeport (medium volatile bituminous) and Pocahontas #3 (low volatile bituminous) coals from the Argonne Premium Coal Sample Program were heated in tetralin for 10 minutes at 430 \pm 5° C. The products were examined by gel permeation chromatography and ^{13}C NMR spectroscopy. Yields for conversion of the coals to THF-soluble products were determined. Yields and GPC characteristics of products from direct extraction of the coals with THF were determined. The most reactive coal in this group, based on conversion to products below MW 600, appears to be Wyoming subbituminous.

INTRODUCTION

The availability of pristine coal samples from the Argonne Premium Coal Program now makes possible the meaningful comparison of experimental results of spectroscopic studies and reactions between laboratories. In previous work with medium-rank coals, we have examined the structural evolution of thermal degradation products by NMR and gel permeation chromatography (GPC) techniques, and we have characterized the processes of hydrogen transfer and exchange under liquefaction conditions using deuterium labeling techniques(1-3). In this paper we present results of a study of the molecular weight distributions of products liberated from a short (10 minute) exposure of five of the premium coals to thermal decomposition in tetralin at 430 °C, and results of ^{13}C NMR characterization of the fractionated products.

EXPERIMENTAL

Coals. The five coals examined in this study were Pennsylvania Upper Freeport medium volatile bituminous coal (Penn UF), coal ID 101; Wyoming subbituminous coal (WYO), coal ID 201; Illinois No. 6 high volatile bituminous (Ill #6), coal ID 301; Pittsburgh #8 bituminous coal (Pitt #8), coal ID 401; and Pocahontas

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#3 low volatile bituminous coal (Poc #3), Coal ID 501.

Extraction of Coals with THF. The five coals (4-5 g each) were washed with three 100 mL portions of tetrahydrofuran (THF). The THF solution was filtered through a 0.45 micron Millipore type FH filter, concentrated, weighed, and examined by GPC and NMR.

Reactions of Coals with Tetralin. The reactions of the coals with tetralin were carried out in 3-mL stainless steel vessels described previously.¹ Tetralin (2 mL) and coal (1 g) were added, and the tube was heated for 10 minutes at 430±5 °C in a Tecam SBS-4 fluidized sand bath. The tubes were opened and washed out with THF. The THF solution and solids were filtered with a 0.45-micron type FH Millipore filter. The residue was air dried and weighed. The THF solution containing the coal products and reaction solvent (tetralin and naphthalene) were concentrated on a rotary evaporator to ca. 20 mL and pipetted into ca. 400 mL of hexane, resulting in the precipitation of brown flakes of the coal product. The THF-soluble, hexane-insoluble product (preasphaltenes and asphaltenes (P+A)) was weighed and examined by GPC and NMR spectroscopy. Occasionally, incomplete removal of tetralin and naphthalene occurred. In these cases, the P+A fraction was redissolved in THF and reprecipitated from hexane. THF oxidation products were occasionally encountered, and were removed by precipitation of a THF solution of the P+A fraction by adding ca. 5-mL of the THF solution to about 100 mL water, which removes the water-soluble THF-associated impurities. For examination of the whole coal reaction mixtures by GPC, reaction tubes were washed out with THF, filtered, and examined directly by GPC.

Gel Permeation Chromatography of P+A, Whole Reaction Mixtures and THF Extracts. Gel permeation chromatography was carried out using one 500Å and one 100Å Waters Associates μ Styragel^R column in series, eluting with THF at a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards from 600-17500 MW and with a variety of low molecular weight compounds below MW 400.

¹³C NMR Spectroscopy of Preasphaltenes + Asphaltenes (P+A). ¹³C NMR spectra of the THF-soluble P+A fractions were determined with a Varian VXR-300 operating at 75 MHz. Approximately 250 mg of P+A fraction was dissolved in 3.0 mL THF-d₈ containing 0.1 M Cr(acac)₃. Spectra were acquired using a 90° pulse, 0.8-s acquisition time and a 3-s pulse delay with inverse gated decoupling. The use of 3% Cr(acac)₃ with inverse gated decoupling has been reported⁽⁴⁾ to produce quantitative results for SRC-II liquids with negligible change in aromaticity (f_a) for pulse delays beyond 4 seconds, and an increase in measured f_a of less than 2% between pulse delays of 2 and 5 seconds. To obtain aromatic/aliphatic ratios, the integral of the 50-10 ppm region obscured by the upfield THF-d₈ multiplet was corrected using the integral of the downfield 67.4 ppm THF peak and a carefully determined integral ratio of the two multiplets of the spectrum of a solution of Cr(acac)₃ in THF-d₈. The values of f_a must be considered qualitative since the error for this procedure is probably 5-7%, while the error in the distribution in aromatic structure is lower.

RESULTS AND DISCUSSION

Direct extraction of the coals (Table I) produced 2-12% of THF-soluble product. Ill #6 is unique in its high solubility, whereas the other coals are

normal, exhibiting 2-4% solubility. The bulk of the directly extractable material clearly is of low molecular weight, with 60-90% below MW 600. Ill #6 and Pitt #8 give noticeably greater amounts of material above MW 600 than the other coals (Figure 1).

Reaction of the coals with tetralin for 10 minutes at 430° C produced yields varying from 3% for Pocahontas #3 to 56% for Pittsburgh #8. The yields from the 10-minute reactions are qualitatively in agreement with rank for the various coals. Total conversions are higher for Wyoming subbituminous, Pittsburgh #8, and Illinois #6. Notice in Table II that while Wyoming subbituminous exhibits the highest conversion, it produces only 25% preasphaltenes and asphaltenes. This means that up to 50% of Wyoming subbituminous is converted to hexane solubles (transfer loss and loss of volatiles is included in this upper estimate), making the Wyoming subbituminous by far the most readily converted coal in this group. The difference between conversion and P+A (%) in Table II is the yield of hexane solubles plus transfer loss and water loss, etc. Thus, hexane solubles may be produced in up to 8% (Penn UF), 17%(Poc #3), 19%(Pitt #8), 15%(IL #6) and 50%(Wyo Sub).

GPC data of Table III show that the bulk of THF-soluble products from all coals at short reaction times consists of material below 600 nominal molecular weight. The effectively inert Poc #3 produced primarily low molecular weight materials at both 10 and 40-minute reaction times. The P+A fractions all exhibit significant amounts of higher molecular weight material (Table IV), consistent with the expected characteristics of THF-solubility. Among the high yielding coals, Pitt #8, Wyo Sub, and Ill #6, the P+A fraction of Wyo sub (Table IV) shows the greatest amount of product below MW 600, consistent with the much greater apparent yield of hexane-solubles discussed above for Wyoming subbituminous. GPC data for extracts of raw coals, total reaction mixtures, and preasphaltene + asphaltene subfractions are depicted in Figure 1.

¹³C FTNMR spectra of P+A fractions determined for the five coal extracts are presented numerically in Table V. THF solubility and hexane solubility tends to produce material of high polarity and rather similar NMR characteristics in the preasphaltene + asphaltene subfraction. The ranges of Table V correspond roughly to phenolic and aryl ether CO (168-148 ppm), substituted aryl C (148-129.5 ppm) and protonated aryl carbon (129.5-110 ppm), the latter group including protonated aryl carbon adjacent to aryl CO structure(5). Within the range of probable error, Table V results indicate higher aryl oxygen content for IL #6, Wyo Sub, and Pitt #8 than for Penn UF and Poc #3, and higher ring substitution for Poc #3.

The results of this paper provide quantitative data for estimation of the amount and structural distribution of products from short residence time liquefaction of the Argonne Premium Coals. A more detailed spectroscopic study of the organic structure of the Argonne coals is presently underway.

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Table I. Direct Extraction of Coals with THF

Coal	Wt. Coal Extd.	Wt. Extract	Wt. %
Ill #6	4.11 g	0.50 g	12%
Penn UF	4.36 g	0.07 g	2%
Wyo Sub	3.97 g	0.12 g	3%
Pitt #8	3.07 g	0.13 g	4%
Poc #3	4.77 g	0.10 g	2%

Table II. Asphaltene + Preasphaltene Yields from Coals^a

Coal	Wt. Coal	Wt. Residue	Wt. P+A	%P+A	Conversion ^b
Penn UF	5 g	3.1 g	1.5 g	30%	38%
Poc #3	1 g	0.8 g	0.03 g	3%	20%
Poc #3 ^c	3.5 g	2.0 g	0.6 g	17%	43%
Pitt #8	4 g	1.0 g	2.24 g	56%	75%
Wyo Sub	4 g	1.0 g	1.0 g	25%	75%
Ill #6	4 g	1.7 g	1.0 g	43%	58%

^a10 minutes, 430 ± 5 °C.

^bbased on recovered coal ((Wt. Coal-Wt. Residue)/Wt. Coal), includes transfer losses, hexane-soluble products not included in P+A, and water losses.

^c40 minutes, 430 ± 5° C

Table III. GPC Data For THF-Soluble Products of Coal-Tetralin Unfractionated Reaction Mixtures

Coal	Area % MW Above 8500	Area % MW 8500-600	Area % MW Below 600
Ill #6	3.9	17.3	78.8
Ill #6 ^a	0.3	13.2	86.5
Pitt#8	5.9	35.0	59.1
Penn UF	1.0	28.1	70.9
Wyo Sub	0.6	25.3	74.1
Poc #3	0.5	7.8	91.7
Poc #3 ^b	0.6	11.0	88.4

^aCoal was pre-extracted with THF before reaction

^b40-minute reaction time

Table IV. GPC Data for P+A Fractions from Premium Coals

Coal	Area % MW above 8500	Area % 8500-600	Area % Below 600
Ill #6	3.4	38.6	58
Pitt #8	5.6	52.8	41.5
Penn UF	7.2	44.0	48.7
Wyom Sub	3.1	31.3	65.6
Poc #3	3.2	40.3	56.4
Poc #3 ^a	0.7	13.7	85.7

^a40-minute reaction timeTable V. ¹³C Spectroscopic results from P+A fractions

Coal	Distribution of Aromatic C %, ppm range			Aromaticity ^a , %
	168-148	148-129.5	129.5-110	
Ill #6	10	44	46	81
Wyo Sub	12	41	47	76
Poc #3	7	55	38	ND
Pitt #8	10	43	47	80
Penn UF	7	34	59	70

^aEstimated error ±5%

Table VI. GPC Data of THF Extracts of Premium Coals

Coal	Area % MW Above 8500	Area % MW 8500-600	Area % MW Below 600
Ill #6	1.6	30.6	67.9
Pitt #8	5.1	31.9	63.1
Penn UF	0.2	10.9	89.0
Wyo Sub	0.4	7.7	92.0
Poc #3	0.1	9.6	90.0

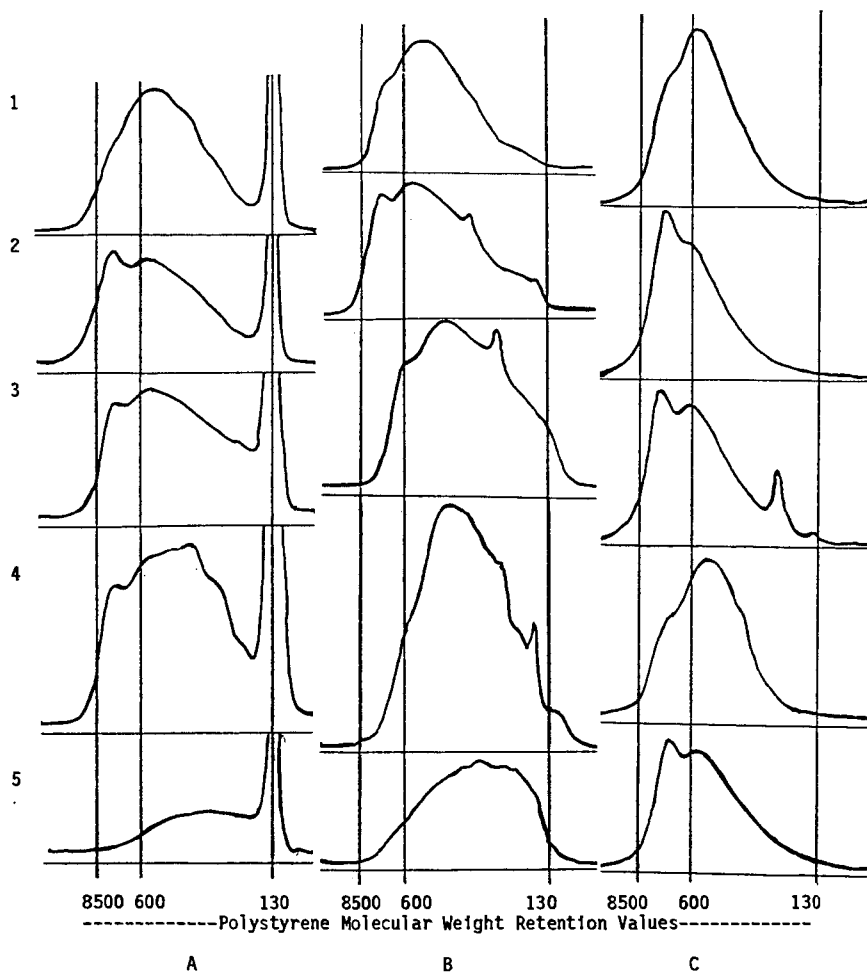


Figure I. Gel Permeation Chromatography Traces for A) Unfractionated Coal/Tetralin Reaction Mixtures; B) Products of THF extraction of the raw coals, and C) THF-Soluble, Hexane-insoluble Products (Preasphaltenes and Asphaltenes). The coals are Row 1, Illinois #6; Row 2, Pittsburgh #8; Row 3, Pennsylvania Upper Freeport; Row 4, Wyoming Subbituminous; Row 5, Pocahontas #3

REACTION OF PREMIUM WYODAK SUBBITUMINOUS COAL WITH POTASSIUM-CROWN ETHER REAGENT

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INTRODUCTION

Coal conversions typically involve reacting coal under severe conditions of temperature and pressure. As a result, bond cleavage is nonselective and often accompanied by retrogressive (bond forming) reactions. This has resulted in less than satisfactory results in deducing coal structure, coal behavior, and reactivity. Incorrect model of the basic structural units of the coal, and the nature of the linkages joining these units have been postulated. In our laboratory, we are studying the solubilization of coal at ambient temperatures and pressures using a site-specific reagent potassium-crown ether (K-CE), and the characterization of the soluble coal oligomer fragments (1,2). The small size and high reactivity of the solvated electrons generated by the K-CE reagent, promotes cleavage reactions at ether (3-5), ester (9), and diarylethane linkages (6,7), resulting in depolymerization and solubilization of coal. Reduction of aromatic rings to dihydro and tetrahydro analogs also occur (2,8). In this paper we report on the solubilization of a Wyodak premium subbituminous coal using K-CE reagent. The characterization of the solubilized coal fragments by IR, NMR, GPC, and microanalysis, is described.

EXPERIMENTAL

Material

Premium Wyodak subbituminous coal (-20 mesh, C=74%, H=5.1%, O=20%, S=0.5%) was obtained from the Argonne Premium Coal Sample Bank, Argonne National Laboratory, IL. Coal samples were used immediately upon opening the glass ampoule. -100 mesh coal used in our study was prepared by grinding the -20 mesh coal in a glove box under liquid nitrogen. The coal was then dried under vacuum for three hours and used immediately for the K-CE reactions.

Reaction of Wyodak Coal With K-CE Reagent

The stoichiometry of the reagents, and the experimental conditions for the coal-K-CE reaction followed established procedure as reported earlier (1,2). The work-up procedure for the reaction is shown in Figure 1.

NMR Spectroscopic Analysis

Proton NMR spectra was obtained from a Nicolet NTC-470 spectrometer (470 MHz) at ambient temperature. Coal samples (20 mg) were dissolved in 0.5 ml of chloroform-d (THF-1

fraction), or DMSO-d₆ (THF-2 and alkali-soluble fractions). Proton decoupled ¹³C NMR spectra were obtained from NTC-200 (50 MHz) at 45°C (22°C for THF-1 fraction). The sample concentration was 50 to 75 mg of sample per 1 ml of NMR solvent. For alkali-soluble fraction NaOD/D₂O was used in the ¹³C NMR experiment.

Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) experiments were carried out on a Waters M-6000A pump with two ultrastayragel columns (500 Å and 1,000 Å) in tandem using THF eluent and a differential refractometer detector. Polystyrene standards were used to obtain a calibration plot. The molecular weight distribution of the THF-soluble coal samples were based on the elution time and the standard calibration plot.

RESULTS AND DISCUSSION

Solubility Studies

The work-up of the coal/K-CE reaction mixture and the extraction of coal into different soluble fractions (THF-1 fraction, alkali-soluble fraction, and THF-2 fraction) are shown in Figure 1. The percent coal solubilized in the various fractions is summarized in Table 1.

Our previous report (2) suggests that the solubility of K-CE treated coal is related to the stoichiometries of the reactants. We found that when the ratio of potassium to coal was decreased, the solubility of coal decreased significantly. We also found that successive K-CE reactions with coal solubilized additional coal. A total solubility of up to 70% was obtained after a coal sample was consecutively treated with K-CE reagent for three to four times. These results suggest that the diffusion of the solvated electrons into the coal matrix is an important factor in determining the solubility of coal, (the amount of soluble coal oligomer fragments formed) after the K-CE reaction.

The present results showed that the diffusion of the solvated electrons is, indeed, an important factor in determining the solubility of the coal, especially the alkali-soluble fraction, in the coal/K-CE reactions. As shown in Table 1, when the coal particle size was changed from -20 mesh to -100 mesh, the alkali-soluble fraction increased from 25% to 47%, whereas the THF-1 and THF-2 fractions did not change significantly. A smaller particle size of coal provides more surface area which allows more of the solvated electrons to react with the aryl ether, ester, and aryl ethane linkages of the coal macromolecule. The alkali-soluble fraction increased two fold on going from a -20 mesh coal particle size to -100 mesh, while the THF-1 and THF-2 fractions were not affected as much. These results suggested that the cleavage of the aryl ether and ester linkages was a predominant reaction during the coal/K-CE reaction.

The alkali-soluble fraction was also subjected to THF extraction. The results are summarized in Table 2. It was interesting to note that the THF extractability of the alkali-soluble fraction from the second K-CE reaction (72%) was higher than that of the first K-CE reaction (55%). During the second K-CE treatment, greater reduction of the polar groups of the coal structure, such as aromatic hydroxyl group to a corresponding less polar dihydro-ketone group, would account for the observed higher solubility in THF.

Elemental Analysis

Elemental compositions of the soluble fractions, the insoluble fractions, and the original premium Wyodak coal are shown in Table 3. The results show that there was an overall increase of the hydrogen content. This hydrogen uptake suggested that Birch-Huckel type

reductions, and cleavage of aryl methylene linkages and ether linkages occurred during the K-CE reaction (7).

THF-1 and THF-2 fractions show relatively high H:C ratios indicating that these fractions are rich in aliphatic material. The THF-1 extraction step (Figure 1) extracted the non-polar hydrocarbon material, that arose from the cleavage of the macromolecular network or was present as trapped molecules. THF-2 step extracted hydrocarbon material containing some polar functionality like OH, or COOH groups (confirmed by high field proton NMR spectroscopy) discussed in the next section. Under alkaline conditions, they are present in salt form (i.e., $-O^-M^+$), and therefore, not extracted during the THF-1 extraction. However, these compounds were not acidic enough (contained more hydrocarbon groups, to make it alkali-soluble). Acidification of the residue converted the salts into the free acid form (O^-M^+ to $-OH$) and this rendered the hydrocarbon material THF extractable.

An oxygen balance of the K-CE reaction is shown in Table 3. The result showed that there was no significant increase or uptake of oxygen during the reaction. This was important to establish because of the distinct presence of a number of oxygen functionalities like carboxylic groups, phenolic $-OH$ groups, and carbonyls in all the extracts. Therefore, the appearance of these oxygen functionalities arose by chemical transformations (cleavage reactions, reductions) of the original oxygen functionalities.

Gel Permeation Chromatography Analysis

GPC was carried out on all the THF-soluble fractions including THF-1 fraction, THF-2 fraction, and THF extract of the alkali-soluble fraction. GPC experiments were expected to yield information on the size (molecular weights and molecular weight distribution) of the various clusters being held together by K-CE cleavable linkages. The absolute molecular weights of the coal extracts were not determined. The results of the GPC analysis are summarized in Table 4.

The results show that K-CE reagent is dismantling the coal macromolecule into low molecular weight, non-polar, hydrocarbon material (THF-1), large (34,000-42,000 and 900-1400) polar oligomer fragments (THF extract of the alkali-soluble fraction), and a second hydrocarbon fraction (MW 1300-2200) containing few polar ($-OH$) functionalities. The results also suggested that upon second consecutive treatment of the coal sample, the size of the resulting coal oligomer fragments are slightly larger than that of the first K-CE reaction. A definite confirmation of these results would require the determination of the absolute molecular weight of the coal extracts.

Infrared Spectroscopy

Infrared spectra of the soluble fractions were obtained and compared to that of the original untreated coal. IR spectra of THF-1 and THF-2 fraction both showed strong absorption at the aliphatic C-H stretching regions, which corresponds well with the finding of the microanalysis. The carbonyl absorption bands (1725 and 1700 cm^{-1}) are found in the IR spectra of all the soluble fractions. These carbonyl absorptions are attributed to the functional groups such as ketone and carboxyl which arose from the reduction of the phenolic OH and the cleavage of the ester groups (2,9).

NMR Spectroscopy Analysis

Proton NMR spectra of the soluble fractions are shown in Figure 2. The spectra of THF-1 and THF-2 fractions (Figure 2A and Figure 2C) confirmed that hydrocarbon material is more abundantly in the THF fractions than in the alkali-soluble fraction. Strong signals at 1.3

ppm and at 1.0 ppm correspond to the methylene protons of long chain polymethylenes and the paraffinic methyl protons respectively. Broad signals at 9-10 ppm and 11-13 ppm corresponding to the phenolic protons and carboxylic protons respectively are found in the spectra of the alkali-soluble fraction and the THF-2 fraction. The broad signals disappeared from the spectra upon the addition of D_2O to the NMR samples thus confirming the presence of these acidic protons. The disappearance of the 4.0 ppm strong broad signal on addition of D_2O to the NMR sample, suggested the presence of aliphatic alcohols. These aliphatic alcohols could arise from the cleavage of the ester linkage of the coal macromolecule.

^{13}C NMR spectra of the alkali-soluble fractions from first and second K-CE reactions are shown in Figure 3. It is interesting to note an increase in the intensity of the peak centered around 110 ppm (corresponding to olefinic carbons) in the spectrum of the alkali-soluble fraction from the second K-CE reaction. The results suggest that during the second K-CE treatment, more of the aromatic ring of the coal oligomer fragments were reduced to the corresponding dihydroaromatics. The spectrum of the alkali-soluble fraction from second K-CE reaction also showed a sharp decrease in the intensity of the alkane carbons resonances.

The proton and ^{13}C spectra of the soluble fractions obtained from the K-CE treated premium Wyodak coal were compared with the proton and ^{13}C spectra of similar fractions of the K-CE treated regular Wyodak coal obtained from Electric Power and Research Institute (EPRI), and stored under water. The spectra are compatible, i.e., the same distinct structural characteristics are observed in the soluble fractions from both the premium Wyodak and regular Wyodak coals.

SUMMARY

In this paper we have shown that a total of 53% premium Wyodak coal was solubilized into THF- and alkali-soluble fractions after the first K-CE reaction. The alkali-soluble fraction accounted for 89% of the total solubles. This result is consistent with our previous findings using the regular Wyodak coal obtained from EPRI. The results showed that a decrease in the coal particle size increased the amount of alkali-soluble coal formed. The oxygen balance, based upon the results of the elemental analysis, showed that the oxygen functionalities (phenolic and carboxylic OH groups and carbonyl groups) found in all the soluble fractions arise by chemical transformations (cleavage reactions, reductions) of the original functionalities.

ACKNOWLEDGMENTS

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Table 1. Solubility of Premium Wyodak Subbituminous

	THF-1 Fraction (%)	Alkali-Soluble Fraction (%)	THF-2 Fraction (%)	Total
One K-CE Reaction ^a	7	25	2	34
Total of Two K-CE Reaction ^a	9	29	6	44
One K-CE Reaction ^a	4	47	2	53

- a. Particle size of coal was -20 mesh.
- b. Particle size of coal was -100 mesh.

Table 2. THF Solubility of Alkali-Soluble Fractions and Total Solubility in THF for Wyodak Subbituminous^a

	% THF Solubility of Alkali-Soluble Fraction	Total % THF Solubility for Wyodak
First K-CE Reaction (20 mesh)	55 (out of 21%)	24
Second K-CE Reaction (20 mesh)	72 (out of 14%)	15
First K-CE Reaction (100 mesh)	53 (out of 47%)	31

- a. THF extraction of untreated Wyodak coal was negligible.
- b. This includes THF-1 and THF-2 fractions, and THF fraction of alkali-soluble.

Table 3. Elemental Analysis of Premium Wyodak Subbituminous and Soluble Fractions* (Moisture and ash-free values)

Coal Samples	C	H	O	N	S	H/C	Yield % ^c	Empirical Formula
Wyodak ^b Subbituminous	74	5.1	20	0.40	0.50	0.83		$C_{100}H_{83}O_{20}$
THF-1 Fraction	77.9	8.9	12.9	0.20	0.36	1.37	7.38	$C_{100}H_{137}O_{12}$
Alkali-Soluble Fraction	71.2	4.9	22.3	0.98	0.59	0.82	25.01	$C_{100}H_{92}O_{23}$
THF-2 Fraction	74.6	7.4	16.8	0.54	0.63	1.19	2.45	$C_{100}H_{115}O_{17}$
Insoluble Fraction	72.1	5.4	21.1	0.89	0.52	0.90	57.82	$C_{100}H_{90}O_{22}$
Total Yield	--	--	--	--	--	--	92.66	$C_{92.7}H_{85.6}O_{19.8}$
Normalised to C_{100}	--	--	--	--	--	--	--	$C_{100}H_{92}O_{21}$

- The results reported here are from first K-CE reaction.
- These values are from the Argonne National Laboratory reported data.
- The solubility % yield from first K-CE reaction.

Table 4. GPC Results of THF Soluble Fractions

	Molecular Weight Distribution		Peak Mol. Wt.
	Number Average \bar{M}_n	Weight Average \bar{M}_w	
First K-CE Reaction^a			
THF-1 Fraction	414	1441	1117
THF-2 Fraction	986	4029	2244
Alk-THF Fraction	23,990	27,170	33,880
	532	1457	930
Second K-CE Reaction^a			
THF-1	641	1981	906
THF-2	1079	4059	1319
Alk-THF Fraction	32,345	35,030	42,204
One K-CE Reaction^b			
THF-1 Fraction	522	1606	956
THF-2 Fraction	1310	4070	1784
Alk-THF Fraction	20,080	24,860	35,714
	1062	2553	1395

- The coal particle size was -20 mesh.
- The coal particle size was -100 mesh.

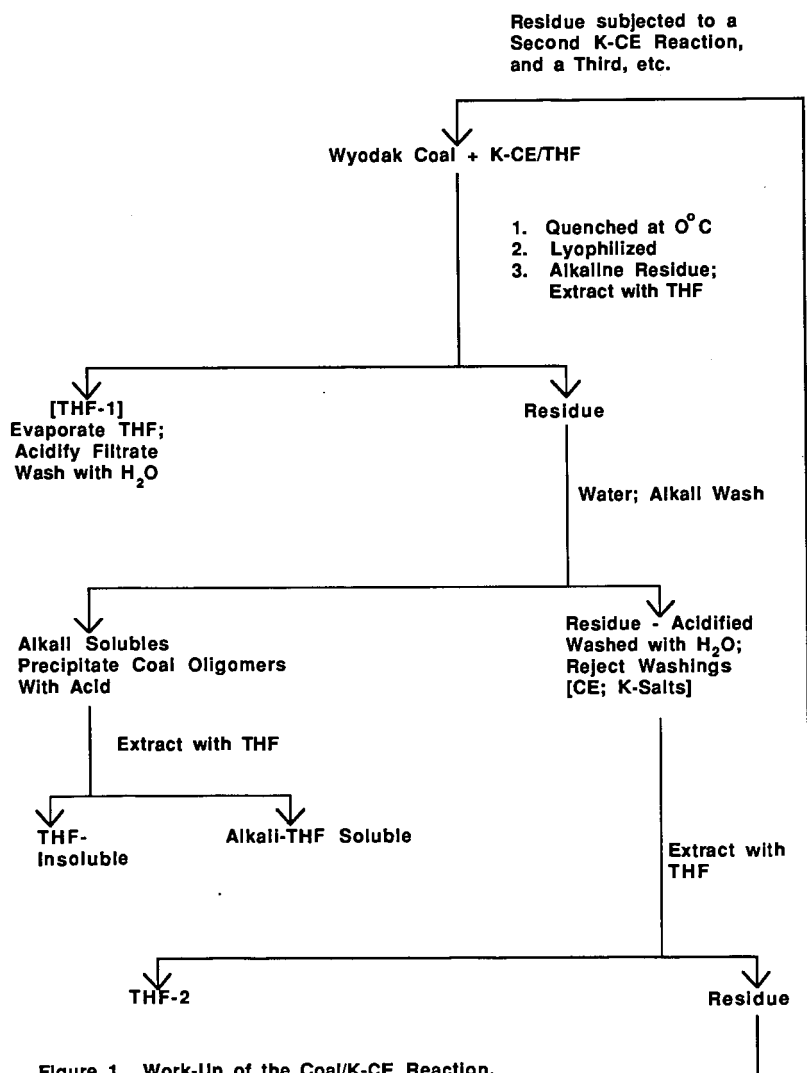


Figure 1. Work-Up of the Coal/K-CE Reaction.

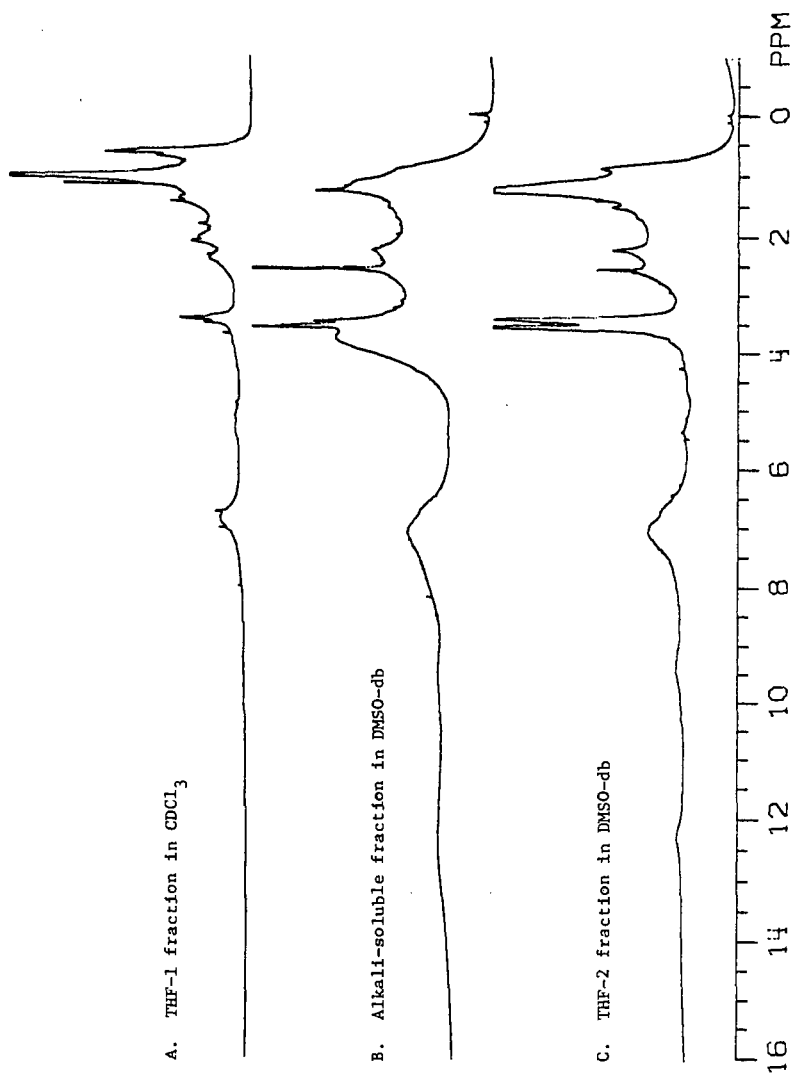


Figure 2. 470 MHz ^1H NMR spectra of soluble fractions of K-CE treated premium Wyodak coal.

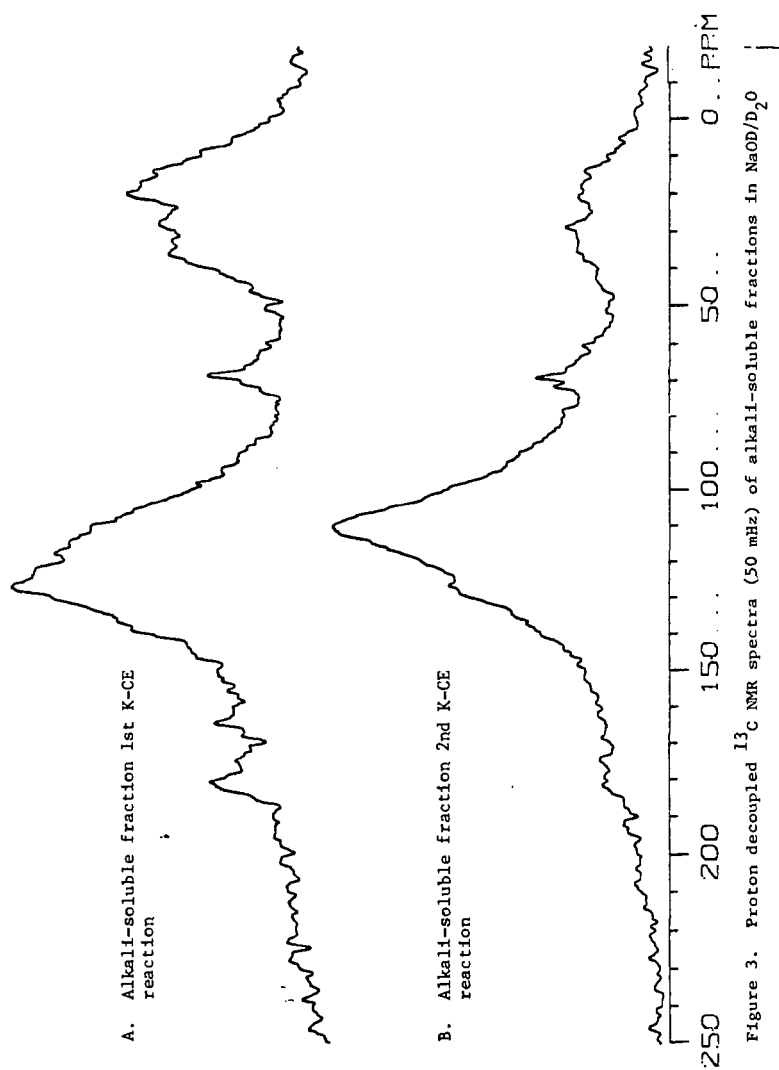


Figure 3. Proton decoupled ^{13}C NMR spectra (50 MHz) of alkali-soluble fractions in $\text{NaOD}/\text{D}_2\text{O}$

CHARACTERIZATION OF THE BENZENE METHANOL EXTRACTS FROM THE ARGONNE PREMIUM COAL SAMPLES

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INTRODUCTION

The Argonne Premium Coal Samples represent a unique opportunity to study a set of pristine samples selected to represent the vast diversity of chemical structures exhibited by U.S. coals. In order to determine if there will be any non-oxidative changes in these coals during long term storage a project has been initiated utilizing a wide range of chemical and physical techniques. One of these techniques meant to focus on any changes which may occur in the volatiles and extractables is described in this paper.

We believe that the material that can be extracted from the coal will provide important information concerning any changes which may occur during long term storage. These materials are easily studied by well established techniques (1-5) and the suggestion has been made that they may be representative of the chemical structures found in the bulk coal (1-3).

EXPERIMENTAL

An overview of the experimental procedures is presented in Figure 1. In order to reduce exposure to atmospheric oxygen all transfers and weighings were performed in a glove box under nitrogen. The Argonne Premium Coal Samples (APCS) used in this study and their elemental analysis are given in Table 1. The preparation of the Argonne Premium Coal Samples has been described by Vorres and Janikowski (6). All of the samples were - 100 mesh except for APCS #2 and #6 which were not available in the smaller mesh size when the work was performed. The coals, excluding the low rank APCS #2 were dried before extraction at 100°C for 16 hours under vacuum then brought to constant weight. APCS #2 was extracted without drying due to possibility that drying would irreversibly modify its physical and chemical structure. The water content of this coal was determined in a separate experiment.

Each coal was extracted in 250 ml. of boiling benzene/methanol (31/69 w/w percent) for 48 hours under nitrogen. The extract was removed by vacuum filtration. The residue was washed with ca. 50 ml. of the benzene/methanol, dried at 100°C under vacuum to constant weight. The benzene/methanol was stripped from the extract at 70°C under vacuum in a rotary evaporator and the extract brought to constant weight.

The extract was then separated into nine fractions using the desorption column chromatographic technique developed by Farcasiu (7). In our application of this technique the extract was dissolved in 7 ml. of the benzene/methanol and coated on 6.65 grams of dried silica gel by evaporating the solvent. The coated silica gel was placed on the top of the column containing 26.8 grams of Aldrich Grade 12 silica gel. This silica gel had

been dried for 8 hours at 120°C and then rehydrated to 4 percent water. The sequential elution solvents in order of use and the classes of compounds reported finding in each fraction are presented in Table 2. A standard volume of 500 ml was used for each elution. In order to correct for silica gel dissolved in each of the fractions, blank elutions were performed under the same conditions as used for the actual separation. The solvent was stripped from each fraction by rotary evaporation under vacuum, and the extract brought to constant weight.

Analysis of each fraction was by Gel Permeation Chromatography (GPC) and Gas Chromatography Mass Spectroscopy. The GPC separation utilized three Ultra Styragel columns with exclusion limits of 1000, 500 and 100 angstroms connected in series to an refractive index and ultraviolet detector. The tetrahydrofuran mobil phase was pumped through the columns at a flow rate of 1 ml/min. Calibration for the conversion of retention times to molecular weight utilized a series of aromatic compounds ranging from naphthalene (128 g/mole) to erythromycin (734 g/mole). The GCMS separations were performed on a Kratos MS25 instrument with a OV-1701 column.

Solvent swellings of the residues from the extractions were performed using the gravimetric technique utilized by Green et al. (8). Briefly ca. 1.1 grams of the residue from the extraction was placed in a desiccator with the benzene methanol swelling mixture in the base. The solvent mixture was frozen and the desiccator evacuated to remove the air. After thawing the freeze thaw cycle was repeated two more times. The swelling coefficients (weight of swollen coal/weight of unswollen coal) were determined after 36 hours.

RESULTS AND DISCUSSION

The yields of benzene/methanol extractables are plotted versus carbon content in Figure 2. Excluding Wyodak subbituminous coal (APCS #2), the yields decreased with rank in a non-linear manner. The low extractability of Wyodak, relative to the trend defined by the higher rank coals, may be attributable to two factors. This coal contains a much higher oxygen content. Thus, the extractables from this coal should be more polar and exhibit a greater propensity towards intramolecular hydrogen bonding than extractables from coals of higher rank. The relatively non-polar benzene/methanol may be incapable of solvating the potentially extractible material. The solvent swelling coefficient (Figure 6) for this coal indicates that benzene/methanol does not show a disparity in its ability to gain access to the macromolecular structure. The Wyodak coal contained 30.4 ± 0.4 percent water which was the highest water content of all the coals studied. It was also the only coal which was not dried prior to extraction. The water from this coal could have modified the extraction potential of the benzene methanol enough to account for the observed yield. Reproducibilities of the extractions were quite good with standard deviations as indicated by the error bars on Figure 2. ranging from 0.0 to 0.22 percent of the mean extraction yield.

The percentage of the benzene/methanol extract in each of the LC fractions corrected for dissolved silica gel is presented in Figure 3. The solvent or mixture used to elute each of the fractions can be found in

Table 2. Only fractions 2, 5 and 6 appeared to show any rank dependence. Fraction 2 which Farcasiu (7) attributed to small non-polar aromatics was found to contain a homologous series of linear alkenes of even number dominance, having a maximum in their distribution near 20 carbons. This distribution is probably not inherent to the coal, but an artifact of the severe conditions used in removing the solvents from the extracts and LC fractions. Figure 4 presents the total extract in this fraction plotted with respect to carbon content for each of the coals studied. The opposite trend may occur, with a higher percentage of the extract from the higher heteroatom content lower ranked coals eluting in fractions 5 and 6. This trend of a higher percentage of the extractables eluting at higher eluent polarity for lower rank coal is illustrated in Figure 5 where yields are plotted versus fraction number for Upper Freeport and Wyodak coals. Although the trends can easily be seen the errors associated with the measurements are so large that no statistically valid conclusion can be drawn.

The average molecular weight from GPC for LC fractions 2-9 is presented in Figure 6. All of the retention times were within the linear portion of the calibration curve (128-734 grams/mole). One must be careful in assigning molecular weights for GPC retention times for compounds dissimilar to the calibration standards due to the basis of the GPC technique on molecular size rather than molecular weight (9). However, comparisons of intrafraction variation in molecular weight should be valid if similar material is eluted for each sample. The maximum in the molecular weight distribution increased up to fraction 7. Indicating a possible dependence of the LC fractionation technique on molecular size as well as functionality. Above fraction 6 the molecular weight appeared to decrease. Only a small amount of the total extract (<10%) was eluted in these two fractions. No valid intrafraction differences could be observed, due to the similarities in the mean molecular weight values and the relatively large errors associated with the measurements.

The swelling coefficient in benzene/methanol is plotted versus carbon content in Figure 7. It decreases with rank in a non-linear manner up to Upper Freeport coal (APCS #1) at 87.1 percent carbon. The Pocahontas 1v bituminous coal (APCS #5) at 89.6 percent carbon exhibited a statistically significant increase in its swelling coefficient. This break in the swelling trend corresponds to the break in the coalification pattern around 87 percent carbon attributed to a maximum in the macromolecular cross-link density by Larsen and Kovac (10). Standard deviations were found to be less than 0.4 percent of the swelling coefficient indicating a valid difference between the mean values for each of the coals studied.

CONCLUSIONS

Significant differences have been observed in the total amount of material extracted from the Argonne Premium coal samples and the swelling coefficients of the resulting residues. Each generally decreased with increasing carbon content as would be expected. Differences were observed in the amount of the extract proportionating into each of the LC fraction. A higher percentage of the extract from coals of lower rank appeared to elute in the more polar fractions, although the experimental procedure will have to be refined before one can be sure that this conclusion is valid. There did not

appear to be any significant differences between the intrafraction maximum in the molecular weight profile for any of the samples. The data reported in this paper represents baseline values for the benzene/methanol extractables from the Argonne Premium Coals. The next phase of the project will involve the repetition of these experiments in order to determine if any changes are occurring during storage.

ACKNOWLEDGMENTS

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TABLE 1. Composition of the Coals used in this Study.

APCS No.	Coal	% Carbon (dmmf)	Composition
1	Upper Freeport mv bituminous	87.1	C ₁₀₀ H _{75.8} N _{1.48} S _{.26} O _{2.58}
2	Wyodak subbituminous	72.0	C ₁₀₀ H _{95.0} N _{1.19} S _{.26} O _{21.3}
3	Illinois #6 hvC bituminous	77.8	C ₁₀₀ H _{87.9} N _{1.54} S _{1.30} O _{8.8}
4	Pittsburgh No. 8 hvA bituminous	83.4	C ₁₀₀ H _{84.9} N _{1.69} S _{0.40} O _{6.03}
5	Pocahontas lv bituminous	89.6	C ₁₀₀ H _{62.9} N _{1.15} S _{0.17} O _{3.26}
6	Utah Blind Canyon bituminous	75.7	C ₁₀₀ H _{111.0} N _{1.59} S _{0.20} O _{15.16}

TABLE 2. The sequence of solvents used for the elutions of the various LC fractions, and classes of compounds eluted as reported by Farcasiu (7).

Fraction No.	Solvent	Major Components
1	Hexane	Saturates
2	Hexane/15% benzene	Aromatics
3	Chloroform	Polar aromatics, Non-basic N,O,S-heterocyclics
4	Chloroform/10°C diethyl ether	Monophenols
5	Diethyl ether/3% ethanol	Basic nitrogen heterocyclics
6	Methanol	Highly functional molecules (>10 wt% heteroatoms)
7	Chloroform/3% ethanol	Polyphenols
8	Tetrahydrofuran	Increasing O content and increasing basicity of nitrogen
9	Pyridine/3% ethanol	Increasing O content and increasing basicity of nitrogen
10		Non-eluted, unidentified materials

Figure 1. Overview of the experimental procedure.

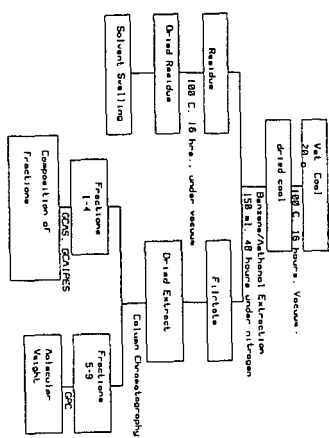


Figure 2. Variation of benzene/ethanol extractables with carbon content, APCS No. in brackets.

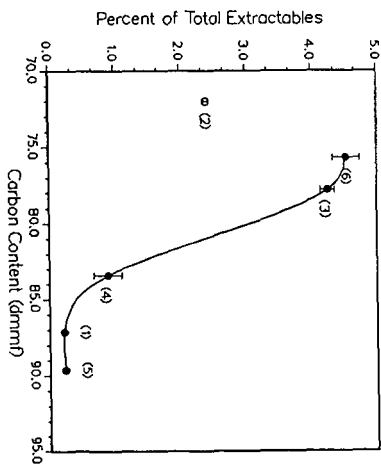


Figure 3. Average percentage of total extractables in LC fractions for APCS #1 - #4.

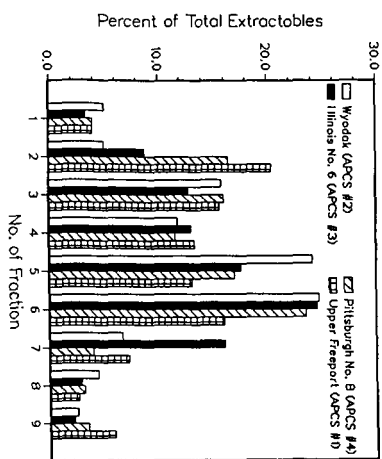


Figure 4. Variation in the percentage of the total extractables in liquid chromatographic fraction with respect to carbon content, the APCS no. is in brackets.

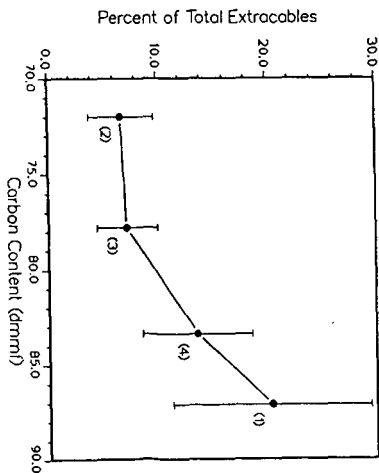


Figure 5. Percentage of total extractables in LC fractions 1-9 for APCS #1 and #2.

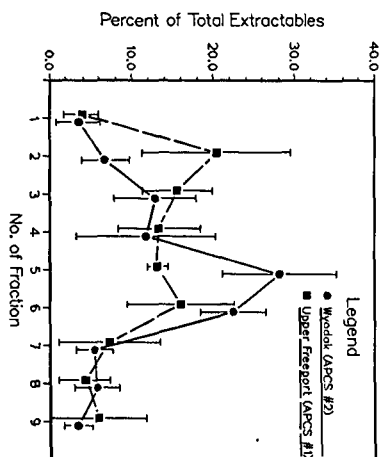


Figure 6. The variation in molecular weight (GPC) with fraction number for APCS 1-4.

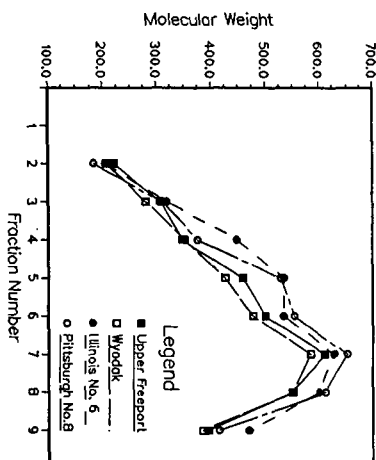
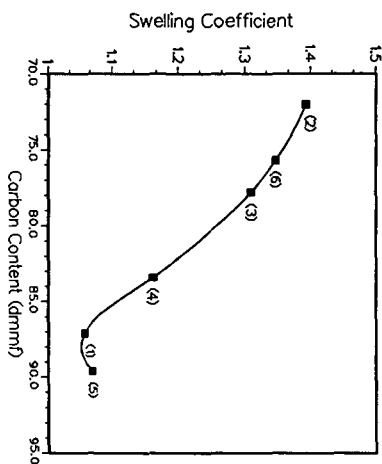


Figure 7. Variation of swelling coefficient in benzene/methanol with carbon content, APCS No. in brackets.



Cobalt Stearate-Aluminum Alkyl Catalyzed Hydrogenation of Illinois
no. 6 High Volatile Bituminous Coal and Model Compounds

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INTRODUCTION

In a previous study, some preliminary results (1) showed that a particular cobalt stearate-aluminum alkyl ($\text{Co}(\text{stearate})_2\text{Et}_3\text{Al}$), [I], homogeneous transition metal complex related to Ziegler catalysts was a very effective hydrogenation promoter under mild temperature conditions ($50\text{--}100^\circ\text{C}$) and hydrogen pressures of from $500\text{--}1000$ psi. Initial results indicated significant yields of gasoline-light oil products from solvent refined coal at 90°C and hydrogen pressures of 700 psi. Ziegler catalysts are not often used for hydrogenation and are rarely employed for coal hydrocracking. However since they have been shown to hydrogenate olefins (2) and aromatic compounds and are Lewis acids, it seems possible to use them in some instances as hydrocracking catalysts. Besides our earlier findings for [I], Dinh et al. (3) have also described selective hydrogenation of naphthalene by Ziegler type catalysts consisting of metal stearates, acetylacetonates and aluminum alkyls. For example hydrogenation of naphthalene using a nickel stearate - AlEt_3 catalyst (5:20 mole equivalent ratio of $\text{Ni}/\text{Et}_3\text{Al}$) yielded 93% tetralin at 150°C and 44 psi, while the use of cobalt acetylacetonate - AlEt_3 (5:25) yielded 99% tetralin at 150°C and 145 psi in an eight hour reaction period. Other Ziegler hydrogenation catalysts have been reported to promote the hydrogenation of aromatic compounds but under more drastic conditions. The complexes of triethylaluminum with $\text{Co}(2\text{-ethylhexanoate})_2$ and $\text{Ni}(2\text{-ethylhexanoate})_2$ have been used to produce 100% conversion (2) of naphthalene [II] to decalin and tetralin at 210°C and 1000 psi. Both catalysts have also been used with benzene, a particularly difficult compound to hydrogenate (2, 4).

Studies (2, 4-5) have shown that the reactivity of the catalyst varies with the transition metal and anionic ligand in the order $\text{Ni} > \text{Co} > \text{Fe} > \text{Cr} > \text{Cu}$ and $2\text{-ethylhexanoate} > \text{benzoate} > \text{acetoacetate} > \text{acetate} > \text{chloride}$ respectively. This roughly follows the order of solubility of the transition metal salts in the hydrocarbon solvents used in the reactions.

Since most of the aromatic structures studied consisted of one, two and three ring units, the Ziegler catalysts used as hydrogenation catalysts should successfully add hydrogen to the aromatic rings in coal. Significantly, aromatic compounds such as naphthalene [II] and polynuclear nitrogen heteroaromatic compounds such as quinoline [III] are found to occur in coal and oil shale. The selective hydrogenation of these materials to form additional useful compounds i.e., naphthalene [II] to form 1,2,3,4-tetrahydronaphthalene [IV] would provide an alternate use of a rather abundant natural resource. Recently, it has been reported (6) that quinolines and isoquinoline can be selectively hydrogenated in the nitrogen-containing ring to form 1,2,3,4-tetrahydroquinoline [V] and N-formyl-1,2,3,4-tetrahydro-

isoquinoline by means of a carbon monoxide and water mixture in the presence of a catalytic amount of rhodium carbonyl cluster at 150°C, 800 psi hydrogen and with stirring for 24 hr. We wish to report that similar hydrogenation of naphthalene [II], quinoline [III], 2-methylquinoline, and isoquinoline can be carried out using catalyst [I] under somewhat milder conditions but no hydrogenation occurs for nitro- or chloro substituted quinolines. We will also discuss the results of using catalyst [I] to hydrogenate Illinois no. 6 coal from the premium coal sample program.

EXPERIMENTAL

The catalyst system [I] for the hydrogenation of the model compounds, was prepared by the addition of 2.2 mmol of triethylaluminum in a dry N₂ atmosphere to a suspension of 1.9 mmole cobalt stearate in hexane. The black catalyst mixture was transferred under dry N₂ to a bomb reactor and 31 mmol of substrate was added. The reactor was pressurized to the desired pressure and heated to the value given in Tables I and II. The products were

Table I. Hydrogenation of naphthalene (II) with the Co(stearate)₂-Et₃Al Catalyst

Time/h	Conditions		Tetrahydro-naphthalene (IV)	% Yield*	
	Temp °C	Pressure Psi		Cis-Decalin	Trans-Decalin
16	90	700	95	-	-
7	90	700	95	3	1
16	90	300	5	-	-
16	22	700	94	3	1
16	45	700	90	6	2

*based on GC analysis.

Table II. Hydrogenation of nitrogen heteroaromatic by Co(stearate)₂-Et₃Al Catalyst.

Substrate	Conditions*	% Yield		
	Temp	A	B	C
quinoline (III)	90	66	21	0
isoquinoline	RT	73	--	27
	90	70	--	
2-methylquinoline	RT	--	--	100
	90	76	--	
8-nitro-2-methylquinoline	RT	44	--	52
	90	--	--	100
4-chloro-2-methylquinoline	90	--	--	100
5-nitroquinoline	90	--	--	100

A) 1,2,3,4-tetrahydro product.

B) 5,6,7,8-tetrahydro product.

C) remaining starting material.

*all reactions were carried out at 700 psi pressure for 16 hrs.

purified by either distillation under reduced pressure or by running the crude products through a silica gel column (chloroform). NMR spectra of the products were recorded on a 60 MHz Varian EM 360L spectrometer. Gas chromatography analyses of products were performed on a Hewlett-Packard 5790 A Series chromatograph using ultra cross-linked methyl Silicon gum column (25 m x 0.2 mm x 0.33 μ m film thickness).

The hexane solvent was stored and distilled from Na/benzophenone. Naphthalene was used as purchased, however quinolines were dried over MgSO_4 , filtered, and vacuum distilled. All reactions were carried out in a 150 cm^3 capacity stainless steel high pressure bomb reactor that could be varied in temperature. The preparation of the catalyst, the assembly of the bomb reactor, and the preparation of the reactants were all carried out under nitrogen in a dry box. The yield of hydrogenated product from naphthalene and quinolines is given in Table I and II for some typical runs.

Hydrogenation of Illinois no. 6 premium coal was also carried out using catalyst [I]. In a typical experiment, 5 g. of coal was added to the catalyst, prepared as described before, in hexane (35 cm^3) in a bomb reactor. The bomb reactor was heated at 90°C under hydrogen pressure of 800 psi and shaken for 24 hrs. The bomb reactor was cooled to room temperature and gas samples collected for analysis. Mass spectrometer-GC analysis of the gaseous products was carried out on a Hewlett Packard 5890 GC/MS system using a J&W DBS thick film column (5 μ m) (12 m x 0.32 mm I.D.). The bomb reactor was then depressurized and a sample of the crude product was filtered through cotton wool or Celite. NMR analysis of the filtrate was carried out in hexane or after removal of hexane.

RESULTS AND DISCUSSION

A. Model Compounds

The NMR spectrum for the hydrogenation of II was in agreement with the spectrum previously recorded for IV. GC analysis of the crude products in Table I shows that naphthalene was hydrogenated selectively at room temperature and at 90°C with only negligible amount of decalin produced. It is important to note that if the hydrogen pressure is dropped to 300 psi from 700 psi, only a 5% yield of IV occurs, with the other 95% being the starting material. Reducing the temperature from 90°C to room temperature (22°C) does not significantly change the 95% yield of IV. Thus the value of the hydrogen pressure is critical to the hydrogenation of II. Lowering the temperature and changing the length of the reaction has almost no effect on the hydrogenation yield. From Table II, it is seen that III is hydrogenated selectively at room temperature to give 73% yield of V and 27% of III remained intact. However, when the temperature is raised to 90°C, MS/GC analysis revealed 66% yield of V along with 21% yield of 5,6,7,8-tetrahydronaphthalene with no sign of the starting material. 2-Methylquinoline was also hydrogenated to 2-methyl-1,2,3,4-tetrahydroquinoline at room temperature and 90°C with 45 and 76% yield respectively. Isoquinoline on the other hand, can only be hydrogenated at 90°C to 1,2,3,4-tetrahydroisoquinoline (70%); at room temperature no hydrogenation took place and the starting material was recovered completely. Hydrogenation of isoquinoline under water-gas

shift condition (6) produced N-formyl-1,2,3,4-tetrahydroisoquinoline whereas under our catalytic conditions, 1,2,3,4-tetrahydroisoquinoline can be prepared in good yield.

Catalyst [I] failed to hydrogenate compounds such as 5-nitroquinoline, 8-nitro-2-methylquinoline, and 4-chloro-2-methylquinoline. In each case the starting material was recovered. It is thought that functional groups such as nitro and chlorine interact with the aluminum alkyl, a Lewis base, and deactivate the catalyst. It has been reported that nitrobenzene and p-nitrophenol could not be hydrogenated in the presence of a catalyst system made of $\text{Ni}(\text{2-ethylhexanoate})_2\text{-AlEt}_3$ whereas benzene was successfully hydrogenated to cyclohexane at 150-190°C (2).

B. Hydrogenation of Illinois no.6 premium coal

The successful results obtained from hydrogenation of the model compounds suggested the possibility of hydrogenating coal under almost similar conditions. Comparison of the NMR spectrum of the coal hydrogenation product with that of a control experiment (heating the same sample of coal in hexane under similar conditions but in the absence of the catalyst), revealed that more signals appeared in the aliphatic region (3.5-1 ppm) when hydrogenation was carried out in the presence of the catalyst, indicating that some aromatic material was converted to saturated products. However, due to the small quantity of the coal sample, it has been difficult to identify the liquefied mixture. Mass spectrum-GC analysis of the gaseous products on the other hand, showed that methane, ethane, propane, cyclohexane, methylpentane and butane, and a few fragments assigned to unsaturated material had been produced. We regard this attempt at this stage, as a primary study and are planning further investigations under different conditions and more suitable media for coal liquefaction.

SUMMARY

Naphthalene (II), quinoline (III), isoquinoline and 2-methylquinoline can be hydrogenated selectively to form 1,2,3,4-tetrahydronaphthalene (IV) (94% yield) at room temperature, 1,2,3,4-tetrahydroquinoline (V) (73% yield at 22°C), 1,2,3,4-tetrahydroisoquinoline (70% yield at 90°C), and 2-methyl-1,2,3,4-tetrahydroquinoline (76% at 90°C) by use of the Ziegler catalyst $\text{Co}(\text{stearate})_2\text{-AlEt}_3$ in a hexane solvent at a hydrogen pressure of 700 psi. Hydrogenation of Illinois no. 6 coal using catalyst [I] has produced a liquefied product and identifiable gaseous components.

ACKNOWLEDGMENT

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LIQUEFACTION REACTIVITY MEASUREMENTS ON
ARGONNE PREMIUM COAL SAMPLES

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ABSTRACT

Liquefaction reactivities for a suite of 4 coals from the Argonne Premium Coal collection have been measured in tubing bomb batch reactors. The coals span a rank range from low volatile through medium and high volatile bituminous to subbituminous. The coals were liquefied in 4 different vehicles (solvents) namely naphthalene, phenanthrene, tetralin, and 1-methylnaphthalene at 698 K (425 C), 6.2 MPa (900 psi) initial hydrogen pressure, and at 5 and 40 minutes residence times. The rate and extent of conversion to THF- and toluene-solubles was measured, and gas make and hydrogen consumption quantified directly. The data show that, for purposes of reactivity comparisons, conversion to toluene-solubles provides the most appropriate data for relative reactivity ranking purposes. The Wyodak subbituminous coal was found to have the highest rate of reaction of the four coals investigated, while the Illinois #6 high volatile bituminous coal exhibited the greatest extent of reaction (conversion to THF- and toluene-solubles).

BACKGROUND

Measurement and correlation of coal reactivity under coal liquefaction conditions has been investigated for many years. Most studies in this area have attempted to find a single parameter or group of parameters capable of correlating fundamental physical, chemical, and geochemical coal properties with the degree of conversion to solvent soluble products under some set of standard reaction conditions (1-6). The relationship between coal organic and inorganic composition and hydrogenation reactivity has been extensively researched by several groups of investigators, most notably by Fischer et al., Given et al., and more recently by Baldwin et al. (7-21).

The purpose of this study was to examine the reactivity of 4 different coals in four different liquefaction vehicles so that the effect of solvent type on coal reactivity could be elucidated. The goal of this portion of the study was to determine the effect of liquefaction vehicle on the absolute and relative reactivities of four coals representing a broad rank range.

EXPERIMENTAL

Four coals from the Argonne Premium Coal collection were liquefied in four different vehicles. The coals employed for this study were:

Wyodak subbituminous
Illinois #6 high volatile bituminous
Upper Freeport medium volatile bituminous
Pocahontas low volatile bituminous

Properties of these coals are available from Argonne National Laboratory. The vehicles (solvents) employed consisted of both donor and non-donor species:

tetralin
1-methylnaphthalene
phenanthrene
naphthalene

Experimental runs were carried out in a tubing bomb microautoclave reactor system at 698 K (425 C), 6.2 MPa (900 psi) initial hydrogen pressure, and for reaction times of 5 and 40 minutes. Data on the conversion of each coal in each solvent to gas, THF-, and toluene-solubles was collected. Details on the procedures utilized have been described elsewhere (22).

DISCUSSION OF RESULTS

Effect of Vehicle on Liquefaction Reactivity

The objective of this study was to determine the reactivity of these four coals under identical reaction conditions, but in different pure solvents. Conversion to both THF- and toluene-solubles was measured. Our previous work has indicated that THF-soluble data provides a poor measure for liquefaction reactivity while toluene solubility data gives excellent correlation between coal properties and coal reactivity (23).

Data from the liquefaction of these four Argonne Premium coal samples in each of the four solvents are shown graphically in Figures 1 through 4. Figures 1 and 2 present the results for conversion of the coals to toluene-solubles at 5 and 40 minutes reaction time, while the data for THF-solubles is presented in Figures 3 and 4. As indicated in Figures 1 and 2, the absolute magnitude of conversion to toluene-solubles is not a strong function of the choice of liquefaction vehicle as long as the type of vehicle (donor vs. non-donor) remains unchanged. Hence the absolute value of the conversions to toluene-solubles are remarkably similar in phenanthrene, naphthalene, and 1-methylnaphthalene. Switching from a non-donor to a hydrogen donor solvent brings about an increase of 20 to 30% in the absolute value of the conversion to toluene-solubles at both 5 and 40 minute reaction times. This observation simply reflects the difference in rate that exists due to the difference in hydrogenation mechanisms in the two solvent systems. In the one case (the donor solvent tetralin) hydrogen needed to stabilize free radicals or to directly attack and cleave strong bonds in the coal matrix can be supplied directly from a hydroaromatic. When a non-donor is used however, the mechanisms of hydrogen transfer are less direct, and involve hydrogen shuttling and/or formation of radical species by reaction of solvent molecules with molecular hydrogen which then can serve as radical cappers and active bond fission promoter as illustrated by McMillen et al. (24).

While the absolute magnitudes of the conversions are functions of solvent, the relative reactivity rankings are not affected by the nature of the solvent if care is exercised in selecting an appropriate data set for purposes of making reactivity comparisons. Different definitions can be used for reactivity depending on the nature of the processing property of

Interest. From a rate processes perspective, the coal with the highest reaction rate would be judged to be the most reactive, while from a static point of view the ultimate extent of conversion to either THF- or toluene-solubles would be the appropriate measure of reactivity. In all cases regardless of vehicle type, the Wyodak subbituminous coal was the most reactive from a kinetic standpoint (based on the rate of conversion to toluene-solubles). In terms of ultimate conversion (extent of conversion to toluene-solubles), the Illinois #6 high volatile bituminous coal was the most reactive, followed by the Wyodak subbituminous coal and the medium and low volatile bituminous coals. These data show clearly that, over a broad range of coal types and reaction times, the nature of the liquefaction vehicle is not a major factor in determining the inherent reactivity of the coal. Figures 3 and 4 display the problems encountered when attempting to utilize data on conversion to THF-solubles as the measure of liquefaction reactivity. As shown, the reactivity rankings are not the same as for the toluene-soluble data set. Further, the relative reactivities of the four coals in terms of both rate and extent of reaction now are a function of the type of liquefaction vehicle employed. The indicated solvent effects and reactivity reversals exhibited by the THF-solubles data make it extremely difficult to draw any concrete conclusions regarding the effect of coal properties on reactivity.

ACKNOWLEDGEMENTS

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FIGURE 1

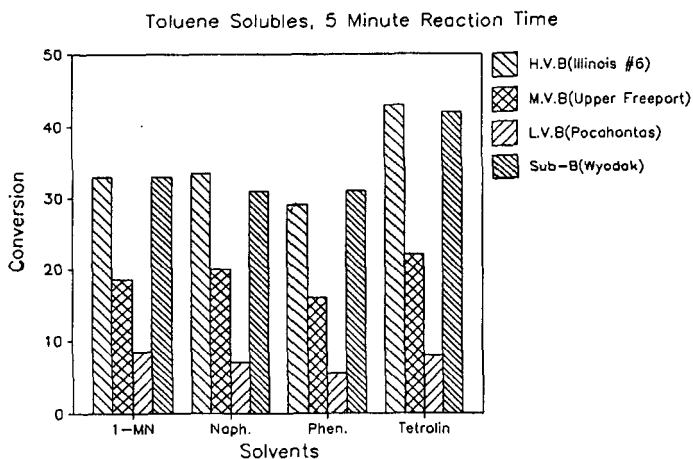


FIGURE 2

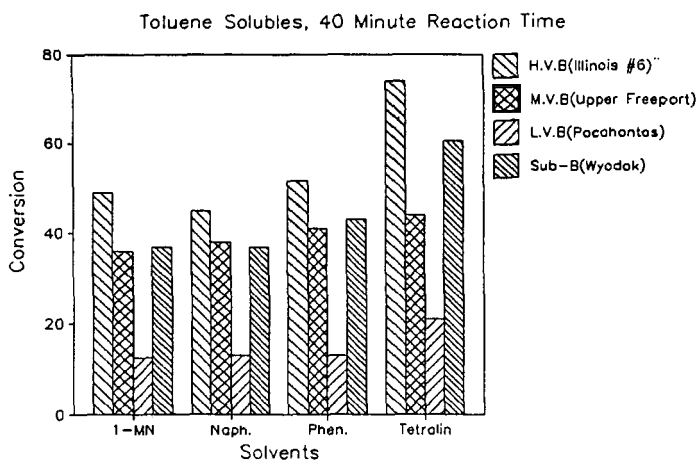


FIGURE 3

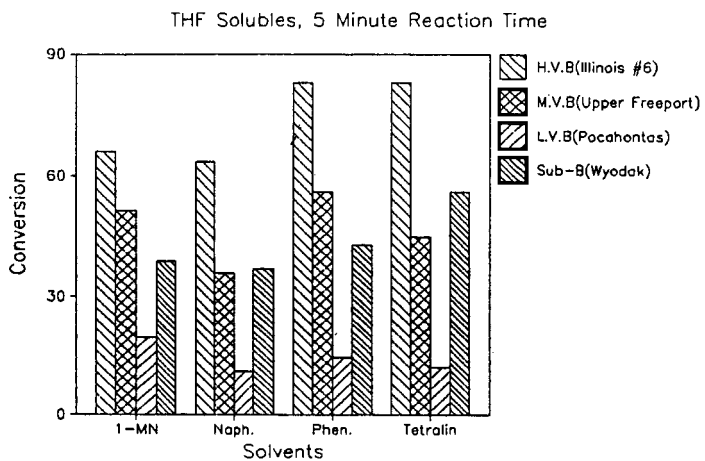
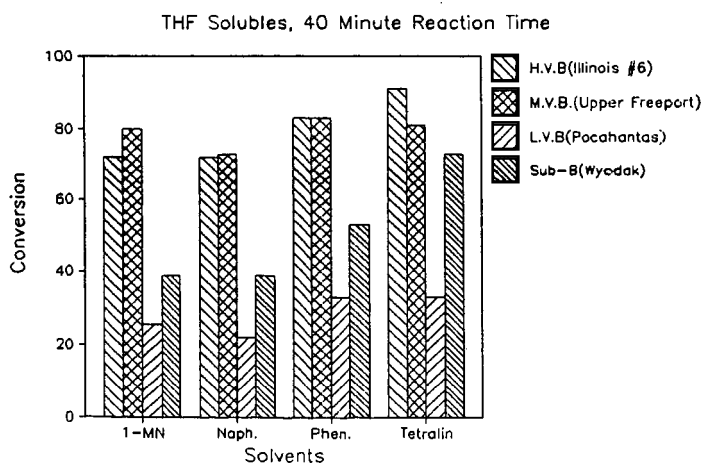


FIGURE 4



**ILLINOIS BASIN COAL SAMPLE PROGRAM AND
ACCESS TO INFORMATION ON ILLINOIS BASIN COALS**

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ABSTRACT

The Illinois Basin Coal Sample Program (IBCSP), was established in 1983 at the Illinois State Geological Survey (ISGS) to facilitate comparisons of results among laboratories conducting basic and applied research on Illinois Basin coal. The sizes of samples available to the individual user and the focus on Illinois Basin coals are distinguishing characteristics of this program. The unit sizes provided to most requesters have been $1/256^{\text{th}}$ of a 55-gallon barrel of coal (nominally 1.5-pound), $1/16^{\text{th}}$ of a barrel (nominally 20-pounds) or one barrel (approximately 400 pounds). The Illinois Coal Development Board (ICDB) and the State of Indiana fund the IBCSP through the Center for Research on Sulfur in Coal (CRSC). The program makes samples available not only to CRSC contractors, but other research groups as well. Additionally, the CRSC supports a computerized information system through which on-line access to data bases on compositions of the IBCSP samples at the ISGS and on research being conducted on these samples is available.

Six Illinois Basin coals, designated IBCSP-1 through IBCSP-6, are available. Three mine-washed Illinois coals became available in 1983: IBCSP-1, a Herrin (Illinois No. 6); IBCSP-2, a Colchester (Illinois No. 2); and IBCSP-3, a mixture of a Springfield (Illinois No. 5) and a Herrin (No. 6). A fourth coal, IBCSP-4, a tipple (run-of-mine) Herrin (No. 6) coal, was added to the program in 1984. The fifth sample (IBCSP-5), a 3-ton channel sample of a Herrin (No. 6), was collected in 1985 and processed into 1-pint cans, 1-gallon cans and 5-gallon cans by Argonne National Laboratory (ANL). This sample is of higher quality than the other five; it was maintained under argon from the mine to the processing facility and all processing was carried out in ANL's inert atmosphere facility designed for the Premium Coal Sample Program (PCSP). IBCSP-5 matches the Illinois coal in the PCSP (PCSP-3). Because the replacement cost for this sample will be very high, charges are made depending on the quantity requested. The sixth sample, provided by the State of Indiana in December 1986, is a mine-washed sample of Springfield (No. 5) Coal from Southwestern Indiana. Multi-ton quantities of the five samples ($3/8" \times 0$) are being maintained in 55-gallon barrels under a low pressure of nitrogen gas at the Applied Research Laboratory of the ISGS in Champaign, Illinois.

Characteristic properties -- maceral composition, reflectance of vitrinite, size and maceral association of pyrite grains, mineral matter composition, and minor and trace element compositions -- were determined on the samples. The informational data base comprising these and other data was established on a mainframe computer at the University of Illinois. The name, address, sample numbers, project title, and project objectives for each project using one or more of the IBCSP samples are included in this data base. To date more than 156 uniform splits of the first four samples in the program have been provided to 67 researchers, 34 located in Illinois. The remainder are in other states and Canada. Telephone requests for information on the IBCSP are received at 217-333-5161.

INTRODUCTION

Coal sample programs, frequently called sample banks, facilitate coal research not only by providing a source of samples but also by simplifying comparisons of results among laboratories that use representative fractions of the same coal. A number of sample programs are in operation in the United States -- the most widely known is the Penn State Coal Bank -- but few provide multi-pound quantities to their users. Additionally, few programs concentrate their efforts on coals from one basin.

In Illinois, the Gas Research Institute, Argonne National Laboratory, Southern Illinois University and the Illinois State Geological Survey are leaders in the development of coal sample programs. The Gas Research Institute (GRI) and the U. S. Department of Energy (U.S.DOE) sponsored a Coal Sample Bank Workshop in March of 1981 to resolve some of the technical problems of establishing a premium coal sample program [1]. The goal was the collection and storage of coal under conditions calculated to preserve as many of the physical and chemical properties as possible. With GRI funding, R. R. Dutcher at Southern Illinois University (SIU) began a study in 1981 on techniques for field acquisition, transporting, processing and storage of premium coal samples. The results are available in the final report [2]. The ANL initiated the Premium Coal Sample Program (PCSP) in late 1982 to meet nation-wide, small-scale, basic-research needs of the research community. A rigid-wall facility was constructed for processing barrel quantities of coal in a nitrogen environment with remote-control equipment [3]. Exceptional care was taken in collection, transport, processing, and storage of the channel samples stored in this program. The relative humidity of the nitrogen atmosphere was controlled to avoid changes in the moisture level. The samples are now available in 5 and 10 gram quantities, hermetically sealed in glass ampules [4].

The Illinois Coal Development Board (ICDB) funds a variety of coal research projects in the State of Illinois. To provide continuity in succeeding years, the ICDB at its first meeting in 1982 expressed interest in funding a project to collect and store reasonably large samples of coal. The board desired to assure the availability of a few of the same coals used by the first year's ICDB contractors for research in subsequent years. The Minerals Engineering Section of the ISGS agreed to collect additional coal and store it at room temperature in a nitrogen atmosphere. The maintenance of samples together with the distribution of samples has become the Illinois Basin Coal Sample Program (IBCSPP). The State of Indiana joined the effort in December 1986 by supplying a sample and becoming a partner in sharing the maintenance and distribution costs.

Five of the six coals in this program have undergone some oxidation before leaving the mine site, during transport to Champaign by truck, and during the time required to crush, riffle and package the samples. For the five coals in question, homogeneity from barrel to barrel was assured by a series of rifflings. For the three-ton lots, the coal was passed through two riffles in succession to produce four sets of four barrels each, each set being equivalent in composition to the other sets. The composition of barrels within a set was not equivalent. In the next stage of riffling, each set was riffled through two riffles in succession to homogenize the four barrels within the set. Added exposure to air was the offsetting cost for this assurance of sample uniformity. For many types of tests, applied bench-scale process testing in particular, the degree of oxidation which occurred is acceptable because all coals entering a commercial process have undergone some degree of oxidation during mining and cleaning. The units delivered to users have been approximately 0.7 kilogram and 11 kilograms (1.5 and 20 pounds). They are produced by riffling a barrel of coal to produce representative fractions. The particle size distribution of the smallest units (1/256th of a barrel) is minus 8 mesh by zero and that of remaining units (1/16th of a barrel or larger) are minus 3/8" by zero. Larger quantities have been supplied to a few projects.

THE SIX COALS AVAILABLE

The six coals now available are described in Table 1. The results of most of the standard ASTM tests are shown in Table 2. The minor and trace elements were also determined (Table 3).

Chemical analyses

Barrel to barrel variations in the initial composition are small based on the analyses of fractions taken during a pilot testing of the homogenization procedure and by the analyses shown in Table 4 (column 1) from riffled fractions of four barrels of IBCSP-4 at the time of the initial packaging. Variations are not more than expected for the analysis of a given sample by different analysts or by different laboratories. Periodic proximate and ultimate analyses show excellent uniformity. Analyses over a two year period for IBCSP-4 in Table 4 are typical. All samples except IBCSP-5, which was specially prepared and prepackaged under nitrogen, can be expected to contain the trace amounts of elemental sulfur shown to accompany oxidation [5].

Minor and trace element analyses

Comparison of the results of minor and trace element analyses with the average of concentrations found in channel samples collected by the ISGS from the Herrin and Springfield seams in Illinois for many years [6], (see Table 3) indicates IBCSP-4 is notably rich in SiO_2 , MgO , Na_2O , F , and Rb . The reason for these high values is the relatively high abundance of mineral matter in this run-of-mine sample. It should also be noted that IBCSP-2 contains a relatively high amount of As , Ge , and Pb compared to the average. Germanium is probably associated with the organic matter in the sample, while As and Pb are probably in pyrite.

Petrographic Analyses

On a mineral matter free basis, all six samples are rich in vitrinite (85 to 90 vol %). On this basis, IBCSP-5 contains the most inertinite group macerals (10 vol %). The reflectance of vitrinite (macerals telocollinite) is highest for IBCSP-3 (0.74 %, mean-maximum) and the other samples range between 0.46 to 0.67 percent. Complete analyses were reported by Harvey, et al. [7].

Mineral matter analyses

The total amount of mineral matter is most abundant in IBCSP-4 because this sample is a run-of-mine product and it contains some shale from the mine roof. A trace of marcasite, an orthorhombic form of FeS_2 , was detected in all samples except IBCSP-4. Two different carbonates, calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$), occur in IBCSP-5. The differences in the mineral phases in the samples may affect the outcome of desulfurization or cleaning processes applied to these coals. Complete analyses are given in Harvey, et al. [7].

Pyrite size and maceral association

The mean diameters for pyrite grains in the six IBCSP samples range from 4 μm (IBCSP-3) to 9 μm (IBCSP-4). The distribution of particle sizes in each sample is much wider than one might project from these mean values and significant differences exist in the way pyrite is distributed among the particles. These differences determine the effectiveness of physical methods for removing pyrite. Approximately 25 percent of the pyrite in IBCSP-5 occurs within macerals-rich particles versus 80 percent in IBCSP-3 [4].

Table 1. Samples available (ash and sulfur on a moisture-free basis)

Sample no.	Product	Seam	Location	Rank	Ash ¹ %	Sulfur ¹ %
1	Prep plant	Illinois No. 6	W. Central IL	HVCB	10.3	4.3
2	Prep plant	Illinois No. 2	Western IL	HVCB	6.7	3.2
3	Prep plant	80% Illinois No. 5 20% Illinois No. 6	Southern IL	HVBB	8.4	2.3
4	Run-of-mine	Illinois No. 6	Southwestern IL	HVCB	38.1	4.2
5	Channel	Illinois No. 6	Southwestern IL	HVCB	18.0	4.6
6	Prep plant	Indiana V ²	Southwestern IN	HVCB ³	9.0	3.8

¹ Analyses in February 1987² The Springfield (Illinois No. 5) Coal is called Indiana V in Indiana³ Borderline between HVBB AND HVCBTable 2. Average¹ analyses² of the six coals in the IBCSP
(values reported on a moisture-free basis except for moisture)

/Sample number	1	2	3	4	5	6
Moisture	14.14	13.62	5.36	10.21	9.47	10.42
Volatile matter	44.12	43.34	39.20	30.56	40.38	39.56
Fixed carbon	45.62	49.92	52.48	31.36	41.61	51.44
H-T ash	10.28	6.66	8.36	38.10	18.00	9.00
Carbon	67.66	73.31	73.82	45.97	63.26	71.64
Hydrogen	4.86	5.21	4.94	3.46	4.40	4.73
Nitrogen	1.18	1.47	1.68	0.80	1.23	1.78
Oxygen (by difference)	11.63	10.09	8.75	7.43	8.39	9.05
Sulfatic sulfur	0.06	0.10	0.09	0.10	0.00	0.0
Pyritic sulfur	1.20	2.34	1.03	2.33	2.55	1.83
Organic sulfur	3.00	0.92	1.16	1.76	2.08	1.94
Pyritic/organic S ratio	0.40	2.53	0.89	1.32	1.23	0.92
Total sulfur	4.26	3.23	2.27	4.19	4.63	3.77
Chlorine	0.13	0.03	0.18	0.05	0.09	0.03
Calorific value (Btu/lb)	12606	13526	13437	8492	11522	13248
Free swelling index ³	4.5	4.3	5.2	2.1	3.8	4.7

¹ Average of all analyses through December 1986 for IBCSP-1 through IBCSP-5.
Average of 10 analyses in February 1987 for IBCSP-6² All values are percent except for pyritic/organic sulfur ratio, calorific values and FSIs³ FSIs are normally reported to the nearest 0.5 unit

Table 3. Minor and trace elements

	IBCSP sample number					Average IL coal*
Oxide/element	1	2	3	4	5	
Minors (%)						
SiO ₂	4.6	1.8	4.1	22.1	8.2	5.5
Al ₂ O ₃	1.6	0.9	1.8	6.5	2.9	2.5
Fe ₂ O ₃	1.7	2.8	1.5	3.8	3.4	2.7
MgO	0.09	0.038	0.073	0.529	0.185	0.046
CaO	0.5	0.2	0.1	1.4	1.2	1.0
Na ₂ O	0.139	0.0182	0.0297	0.337	0.168	0.0987
K ₂ O	0.21	0.11	0.2	0.99	0.33	0.22
P ₂ O ₅	0.02	0.01	0.03	0.09	0.02	0.02
TiO ₂	0.08	0.03	0.09	0.31	0.15	0.11
Traces (ppm)						
Ag	<1	<1	<1	<1	<0.2	0.06
As	2	32	16	5	2.6	11
Ba	32	14	28	135	73	140
Be	1.4	3.3	1.2	2.7	1.0	1.5
B	193	109	71	317	179	118
Br	6	3	12	3	6.5	12
Cd	1.1	0.8	0.1	<0.4	-	1.5
Ce	6	2	10	21	19	14.7
Co	3	6	5	9	3.8	5
Cr	31	7	16	44	19	18
Cs	1.1	0.8	1.2	4	1.9	1.0
Cu	9.7	21.9	8.0	14.4	9.5	12.5
Dy	0.6	1.5	0.9	1.7	-	1.1
Eu	0.2	0.2	0.2	0.5	0.2	0.3
F	63	26	56	460	-	68
Ga	3	3	3	10	3.4	3.9
Ge	<5	30	<5	<5	5	5
Hf	0.4	0.2	0.5	1.7	1.0	0.6
La	4	2	7	16	5.9	7
Li	11.3	18.1	29.9	38.9	8.2	16.3
Lu	0.1	0.1	0.1	0.3	0.08	0.1
Mn	31	16	13	112	71	55
Mo	15	4	13	6	9	9
Ni	11	22	14	23	15	18
Pb	8	149	57	28	6	28
Rb	9	5	11	63	20	16
Sb	0.2	3.4	1.1	0.3	0.3	1.0
Sc	2.1	2.1	2.6	6.4	2.4	2.7
Se	1.5	1.3	2.2	2.2	2.4	2.4
Sm	0.9	0.9	1.4	2.9	1.2	1.4
Sn	<1	<1	<1	1.7	<5	-
Sr	25	12	33	58	29	34
Ta	0.1	0.1	0.1	0.4	0.25	0.2
Tb	0.1	0.2	0.2	0.2	0.13	0.2
Th	1.2	0.7	1.3	3.9	3.2	2.2
Tl	<2	<2	<2	<2	1.0	1.0
U	<2	<1.5	<4	<3	1.2	1.5
V	25	22	26	50	23	31
W	<0.5	<0.5	<0.7	0.9	1.5	0.6
Yb	0.4	0.6	0.5	1.0	0.5	0.6
Zn	172	99.8	45.1	175	77	248
Zr	16	13	23	51	28	35

* Calculated from data on channel samples from the Herrin (No.6) and Springfield (No. 5) Coals (Harvey, et al., 1983).

Table 4. Analyses of IBCSP-4¹
(values reported on a moisture-free basis except for moisture)

Analysis ²	C22538-41 July 84 Av. (Std. Dev.) ³	C23924 Sept 85	C24450-51 March 86	C24893 July 86
Moisture	10.2 (0.05)	10.2	10.2	10.3
Volatile matter	30.3 (0.17)	30.4	31.2	31.1
Fixed carbon	31.6 (0.27)	31.3	30.8	31.0
Ash	38.1 (0.29)	38.3	38.0	38.0
Carbon	46.92 (0.42)	46.09	48.04	48.00
Hydrogen	3.28 (0.054)	3.44	3.27	3.37
Nitrogen	0.68 (0.045)	1.09	0.80	0.98
Oxygen	6.95 (0.40)	6.82	5.24	5.30
Sulfatic sulfur	0.10 (0)	0.26	0.01	0.0
Pyritic sulfur	2.17 (0.059)	2.36	2.77	2.51
Organic sulfur	1.80 (0.036)	1.61	1.78	1.76
Total sulfur	4.07 (0.071)	4.23	4.55	4.27
Chlorine	0.04 (0.007)	0.03	0.10	0.08
Calorific Value (Btu/lb)	8527 (26)	8407	8462	8469
Free Swelling Index	2.5	2.5	1.5	1.0

¹ Herrin (No. 6) coal (run-of-mine) from a southwestern Illinois underground mine collected December 15, 1983

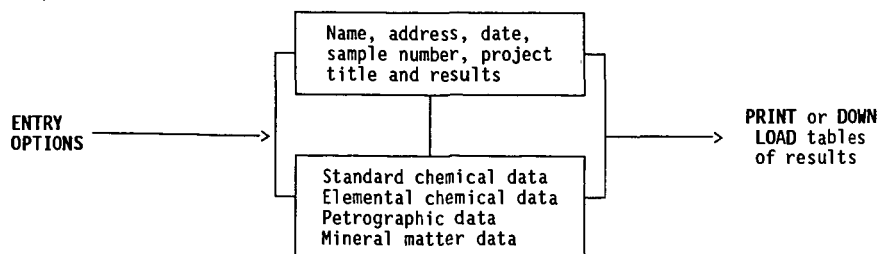
² All values are percent except the calorific values and the FSIs

³ Analyses on riffled fractions from four of the eight barrels

INFORMATION SYSTEM

A computerized information system (data base) is available on a mainframe computer (Control Data, Cyber-175) at the University of Illinois in Urbana. This system operates in parallel with a larger existing data base on the same computer covering the Chemistry of Illinois coals [8]. Both systems can be accessed by an investigator at a remote facility through a modem during a single computer session.

Two types of data files were installed for the IBCSP. The first contains the name, address, project title, and results or objectives of the researchers using the samples; the second contains the chemical and other characteristic properties of the samples:



Names of researchers using these samples and the analytical data can be retrieved. Users of the data base may read about the past and current research on the samples directly at their monitor. Users may also select and obtain hard copy for any type of analytical data or other types of data on a single sample or all six of them. Menu options facilitate downloading retrieved files to the user's own microcomputer. Those who have only a terminal and modem can print retrieved data at the ISGS for mailing to the user. Access to the data base can be obtained by contacting R. Harvey (217-244-0836). A small fee is required to cover the direct computer charges. Persons without terminals can obtain information by contacting either the Coal Section or the Minerals Engineering Section of the Illinois State Geological Survey (217/333-4747) or the Center for Research on Sulfur in Coal (217/333-9241), both located in Champaign, Illinois.

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